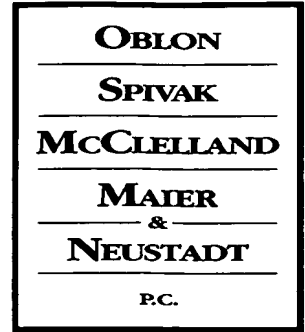




Docket No.: 246578US2

COMMISSIONER FOR PATENTS  
ALEXANDRIA, VIRGINIA 22313



ATTORNEYS AT LAW

RE: Application Serial No.: 10/733,247  
Applicants: Toshiki NANYA, et al.  
Filing Date: December 12, 2003  
For: TONER, DEVELOPER USING THE SAME, TONER  
CONTAINER USING THE SAME, PROCESS  
CARTRIDGE USING THE SAME, IMAGE-  
FORMING PROCESS USING THE SAME AND  
IMAGE-FORMING APPARATUS USING THE SAME  
Group Art Unit: 1756  
Examiner: GOODROW, J. L.

SIR:

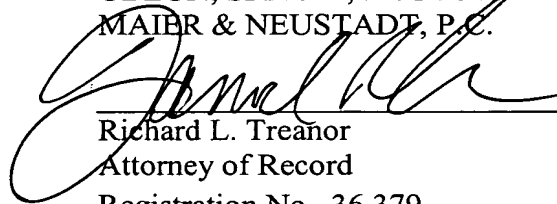
Attached hereto for filing are the following papers:  
**Letter**

**English Translation of Japanese Patent Application No. 2002-363067 w/ Declaration (Executed)**

Our check in the amount of \$0.00 is attached covering any required fees. In the event any variance exists between the amount enclosed and the Patent Office charges for filing the above-noted documents, including any fees required under 37 C.F.R. 1.136 for any necessary Extension of Time to make the filing of the attached documents timely, please charge or credit the difference to our Deposit Account No. 15-0030. Further, if these papers are not considered timely filed, then a petition is hereby made under 37 C.F.R. 1.136 for the necessary extension of time. A duplicate copy of this sheet is enclosed.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Richard L. Treanor  
Attorney of Record

Registration No. 36,379

Customer Number

**22850**

(703) 413-3000 (phone)  
(703) 413-2220 (fax)

Daniel R. Evans, Ph.D.  
Registration No. 55,868



DOCKET NO: 246578US2

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :  
TOSHIKI NANYA, ET AL. : EXAMINER: GOODROW  
SERIAL NO: 10/733,247 :  
FILED: DECEMBER 12, 2003 : GROUP ART UNIT: 1756  
FOR: TONER, DEVELOPER USING THE :  
SAME, TONER CONTAINER USING THE  
SAME, PROCESS CARTRIDGE USING  
THE SAME, IMAGE-FORMING PROCESS  
USING THE SAME AND IMAGE-  
FORMING APPARATUS USING THE  
SAME

LETTER

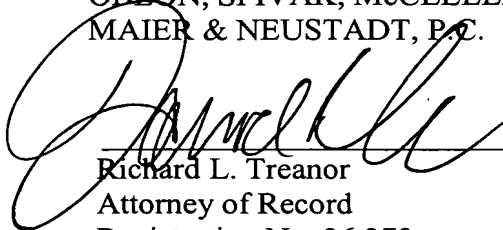
COMMISSIONER FOR PATENTS  
ALEXANDRIA, VIRGINIA 22313

SIR:

Applicants concurrently file an English translation of JP 2002-363067 (JP '067), filed on December 13, 2002. Attached to the English translation of JP '067 is a Declaration by the translator of JP '067 stating that the attached English translation of JP '067 is a true English translation JP '067. Because Applicants have timely claimed priority to JP '067, it is requested that the Examiner acknowledge Applicants' perfection of priority to JP '067.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,  
MAIER & NEUSTADT, P.C.



Richard L. Treanor  
Attorney of Record  
Registration No. 36,379

Customer Number  
**22850**

Tel: (703) 413-3000  
Fax: (703) 413 -2220  
(OSMMN 06/04)

Daniel R. Evans, Ph.D.  
Registration No. 55,868



# DECLARATION

I, Takashi Ota, the translator of the attached document, do hereby certify that to the best of my knowledge and belief, the attached document is true English translation of Japanese Patent Application No. 2002-363067.

Signed, this twenty-third day of March, 2006

A handwritten signature in black ink, consisting of a large loop and a diagonal stroke, positioned above a horizontal line.

Takashi OTA

Ricoh Technology Research Inc.

3-2-3, Shinyokohama, Kohoku-ku,

Yokohama-shi, 222-8530 Japan



Date of Filing: December 13, 2002

Japanese Patent Application No.: 2002-363067

[Name of Document] Application for Patent

[Reference No.] 0205399

[Date of Filing] December 13, 2002

[Addressee] Commissioner of Japan Patent Office

5 [Int'l Class] G03G 5/00

[Title of the Invention] Negative Charging Toner, Developing Agent, Image Forming Method, and Image Forming Apparatus

[Number of Claims] 17

10 [Inventor]

[Address] c/o Ricoh Company, Ltd.  
3-6, Nakamagome 1-chome, Ota-ku, Tokyo

[Name] Toshiki Nanya

[Inventor]

15 [Address] c/o Ricoh Company, Ltd.  
3-6, Nakamagome 1-chome, Ota-ku, Tokyo

[Name] Masami Tomita

[Inventor]

[Address] c/o Ricoh Company, Ltd.  
3-6, Nakamagome 1-chome, Ota-ku, Tokyo

20 [Name] Shigeru Emoto

[Inventor]

[Address] c/o Ricoh Company, Ltd.  
3-6, Nakamagome 1-chome, Ota-ku, Tokyo

25 [Name] Shinichiro Yagi

[Inventor]

[Address] c/o Ricoh Company, Ltd.  
3-6, Nakamagome 1-chome, Ota-ku, Tokyo

[Name] Naohiro Watanabe

30 [Inventor]

[Address] 13, Fujinami, Aza, Kawaji,  
Shinjo-shi, Aichi-ken

[Name] Tadao Takikawa

[Applicant]

[Id. No.] 000006747  
[Name] Ricoh Company, Ltd.  
[Representative] Masamitsu Sakurai

5 [Agent]

[Id. No.] 100074505  
[Patent Attorney]  
[Name] Toshiaki Ikeura

[Indication of Fee]

10 [Prepayment No.] 009036  
[Amount of Payment] 21,000 Yen

[List of Attached Documents]

[Name of Document] Specification 1  
[Name of Document] Drawings 1  
15 [Name of Document] Abstract 1  
[General Power of Attorney No.] 9909722

[Necessity of Proof] Necessary

[Name of Document] Specification

[Title of the Invention] Negative Charging Toner, Developing  
20 Agent, Image Forming Method, and Image  
Forming Apparatus

[Scope of Claims]

[Claim 1]

Negative charging toner obtained by dissolving or  
25 dispersing a toner composition containing a toner binder resin  
including a modified polyester type resin (i) reactible with a  
compound having an active hydrogen group in an organic solvent to  
provide a dissolved product or a dispersed product, dispersing  
the dissolved product or the dispersed product in an aqueous  
30 medium containing a resin fine particle, and simultaneously  
causing to react with the compound having the active hydrogen  
group, and removing the solvent from a thus obtained dispersing  
liquid, the negative charging toner having a storage modulus (G')

of 500 Pa or more at a frequency of 1 Hz and a temperature of 180 °C.

[Claim 2]

The negative charging toner as described in claim 1,  
5 characterized in that the storage modulus ( $G'$ ) at the frequency of 1 Hz and the temperature of 180 °C is in a range of 700 to 7000 Pa.

[Claim 3]

The negative charging toner as described in claim 1 or 2,  
10 characterized in that the toner binder resin contains the modified polyester type resin (i) and a non-modified polyester type resin (ii), wherein a weight ratio of the modified polyester type resin (i) to the non-modified polyester type resin (ii) is in a range of 5/95 to 75/25.

15 [Claim 4]

The negative charging toner as described in any one of claims 1 and 2, characterized in that an acid value of the toner binder resin is in a range of 0.5 to 40 mgKOH/g.

[Claim 5]

20 The negative charging toner as described in any one of claims 1 through 4, characterised in that a glass transition point ( $T_g$ ) of the toner binder resin is in a range of 40 to 70 °C.

[Claim 6]

The negative charging toner as described in any one of  
25 claims 1 through 5, characterised in that the resin fine particle includes any one of a vinyl type resin, a polyurethane resin, an epoxy resin and a polyester resin, or a mixture thereof.

[Claim 7]

The negative charging toner as described in any one of  
30 claims 1 through 6, characterised in that an average particle diameter of the resin fine particle is in a range of 5 to 500 nm.

[Claim 8]

The negative charging toner as described in any one of

claims 1 through 7, characterised in that a volume average particle diameter of a toner particle is in a range of 4 to 8  $\mu\text{m}$ .

[Claim 9]

The negative charging toner as described in any one of  
5 claims 1 through 8, characterised in that a volume average particle diameter/number average particle diameter ( $D_v/D_n$ ) of the toner particle is in a range of 1.10 to 1.25.

[Claim 10]

The negative charging toner as described in any one of  
10 claims 1 through 9, characterised in that an average degree of circularity of the toner particle is in a range of 0.90 to 0.96.

[Claim 11]

The toner as described in any one of claims 1 through 10,  
characterized in that a shape of the toner particle is a spindle  
15 shape.

[Claim 12]

The negative charging toner as described in claim 11,  
characterized in that the toner particle is in the spindle shape  
having a ratio ( $r_2/r_1$ ) of a short axis  $r_2$  to a long axis  $r_1$  of the  
20 toner particle is in a range of 0.5 to 0.8, and a ratio ( $r_3/r_2$ ) of thickness  $r_3$  to the short axis  $r_2$  of the toner particle is in a range of 0.7 to 1.0.

[Claim 13]

The negative charging toner as described in any one of  
25 claims 1 through 12, characterized in that the solvent is removed from an obtained dispersing liquid at least by agitating and/or heating the dispersing liquid.

[Claim 14]

A developing agent, characterized in that the developing  
30 agent includes the negative charging toner as described in any one of claims 1 through 13.

[Claim 15]

An image forming method, characterized in that the

developing agent as described in claim 14 is used in a developing device having a toner recycling mechanism.

[Claim 16]

A container, characterized in that the developing agent as  
5 described in claim 14 is filled.

[Claim 17]

An image forming apparatus, characterized in that the container as described in claim 16 is loaded.

[Detailed Description of the Invention]

10 [0001]

[Technical Field of the Invention]

The present invention relates to negative charging toner for visualizing an electrostatic image formed on a photoconductor surface in electrophotography, electrostatic recording or the  
15 like, a developing agent containing the toner, an image forming method using the developing agent, a container provided by filling the developing agent, and an image forming apparatus provided by loading the container.

[0002]

20 [Background Art]

According to an electrophotographic apparatus, an electrostatic recording device, or the like, an electric or a magnetic latent image is conventionally visualized by using toner. For example, according to an electrophotographic method, an  
25 electrostatic image (latent image) is formed on a photoconductor, subsequently, the latent image is developed by using the toner and thus a toner image is formed (electrostatic image development). The toner image is normally transferred on a transfer material such as paper, and then fixed by a method such  
30 as heating.

[0003]

In general, the toner used for the electrostatic image development is a coloring particle provided by containing a



coloring agent, a charge controlling agent, and another additive in a binder resin, and a method for manufacturing the toner is broadly classified into a pulverizing method and a suspension polymerization method. According to the pulverizing method, the toner is manufactured by melting and mixing the coloring agent, the charge controlling agent, an offset inhibiting agent, or the like in a thermoplastic resin to be uniformly dispersed, and then pulverizing and classifying an obtained composition. According to the pulverizing method, the toner having an excellent characteristic to some extent may be produced, but selection of a toner material is limited. For example, the composition obtained from melting and mixing is to be pulverized and classified by an economically usable device. From the request, the composition obtained from melting and mixing is to be made fragile enough to pulverize and classify. Accordingly, when providing a particle by actually pulverizing the composition, a particle diameter distribution having a broad range is easily formed, and in order to obtain a copy image having a satisfactory resolution and gradation, for example, a fine particle having a particle diameter of 5  $\mu\text{m}$  or less and a coarse particle having a particle diameter of 20  $\mu\text{m}$  or more are to be removed by classification, causing a deficiency that a yield becomes extremely low. Moreover, according to the pulverizing method, the coloring agent, the charge controlling agent or the like is difficult to be uniformly dispersed in the thermoplastic resin. Non-uniform dispersion of a compounding agent adversely affects toner flowability, developability, durability, image quality, or the like.

[0004]

In order to overcome the problems in the pulverizing method, a method for manufacturing the toner according to the suspension polymerization method is proposed and implemented in recent years. A technology for manufacturing the toner for electrostatic latent image development by a polymerization method is publicly known.

For example, a toner particle is obtained from the suspension polymerization method. However, the toner particle obtained from the suspension polymerization method is spherical to produce a deficiency that a cleaning property is inferior. According to development and transfer having a low image area rate, an amount of transfer residual toner is small and a cleaning failure does not become problematic. However, according to development and transfer having a high image area rate such as a photographic image, untransferred toner may be produced on the photoconductor as the transfer residual toner after image formation, and when accumulated, image background stain may be produced. Furthermore, the untransferred toner may contaminate a charge roller for causing the photoconductor to perform a contact charge, or the like, and demonstration of original charge capability may be incapacitated. The inconveniences become more intense if a sheet feeding failure occurs.

[0005]

In order to solve the problem, a method for obtaining an amorphous toner particle by aggregating a resin fine particle obtained from an emulsion polymerization method is disclosed (Japanese Patent Registration No. 2537503).

[0006]

However, the toner particle obtained from the emulsion polymerization method includes a large amount of residual surface active agent not only on a surface but also in a particle even through a water washing step to damage environmental stability of a toner charge and broaden a charge quantity distribution, and thus to produce background stain of an obtained image. Moreover, the residual surface active agent contaminates the photoconductor, the charge roller, a development roller, or the like, and thus demonstration of original charge capability may be incapacitated.

[0007]

Meanwhile, according to a fixing step by a contact heating

system performed by using a heating member such as a heat roller, releasability of the toner particle relative to the heating member (hereinafter referred to as "offset proof property") is required. The offset proof property may be improved by providing a releasing agent on a surface of the toner particle. On the other hand, a method for improving the offset proof property by containing a resin fine particle in the toner particle, in addition, unevenly dispersing the resin fine particle on the surface of the toner particle is disclosed in Japanese Patent Laid-open Publication Nos. 2000-292973 and 2000-292978. However, according to the methods, a fixing lower limit temperature is increased to produce a deficiency that a low-temperature fixing property, namely, an energy-saving fixing property is not sufficient.

[0008]

Moreover, according to the method for obtaining the amorphous toner particle by aggregating the resin fine particle obtained from the emulsion polymerization method, the problem as described below is caused.

Firstly, when aggregating a releasing agent fine particle in order to improve the offset proof property, the releasing agent fine particle is occluded inside the toner particle. As a result, the offset proof property may not be sufficiently improved. Secondly, the resin fine particle, the releasing agent fine particle, a coloring agent fine particle, or the like is randomly fused and the toner particle is formed, and thus a fluctuation is produced for a composition (ratio of containing a constituent), a molecular weight of a constituent resin, or the like among obtained toner particles. As a result, a surface characteristic is different among the toner particles, and thus a stable image may not be formed over a long period of time. Thirdly, according to a low-temperature fixing system where low-temperature fixing is required, fixing inhibition due to a

resin particle unevenly dispersed on a toner surface occurs, and thus fixing temperature range may not be secured.

[0009]

In order to solve these problems, Japanese Patent Laid-open Publication No. 2002-169336 (patent document 1) discloses a method for obtaining an amorphous toner particle by dissolving or dispersing a toner composition containing a toner binder resin including a modified polyester type resin (i) reactible with a compound having an active hydrogen group in an organic solvent, dispersing the dissolved product or the dispersed product in an aqueous solvent containing a resin fine particle, and causing to react with the compound having the active hydrogen group, and removing the solvent from an obtained dispersing liquid. However, according to the method, when a cross-linking reaction or an extension reaction is insufficient, a positive charge property of an obtained toner particle is strong, and such a problem newly occurs as damaging environmental stability of a toner negative charge, broadening a charge quantity distribution, and producing unfavorable background stain of an obtained image.

[0010]

[Patent document 1]

Japanese Patent Laid-open Publication No. 2002-169336

[0011]

[Problems to be Solved]

The present invention is made in view of the circumstances as described above.

A first object of the present invention is to provide toner having a sharp charge quantity distribution of a negative charge property of the toner and capable of forming a clear and excellent visible image over a long period of time.

A second object of the present invention is to provide toner corresponding to a low-temperature fixing system while maintaining a cleaning property, having an excellent offset proof

property, and without contaminating a fixing device and an image.

A third object of the present invention is to provide a developing agent containing the toner, an image forming method using the developing agent, a container provided by filling the developing agent, and an image forming apparatus provided by  
5 loading the container.

[0012]

[Means for Solving Problems]

Inventors of the present invention have made an intensive  
10 investigation. As a result, the present invention is attained by finding that, according to a method for obtaining a toner particle by dissolving or dispersing a toner composition containing a modified polyester type resin reactible with a compound having an active hydrogen group in an organic solvent,  
15 dispersing the dissolved product or the dispersed product in an aqueous medium containing a resin fine particle, and simultaneously causing to react with the compound having the active hydrogen group, and removing the solvent from an obtained dispersing liquid, the compound having the active hydrogen group  
20 in the toner particle needs to be decreased by cross-linking or extending the modified polyester type resin reactible with the compound having the active hydrogen group using the compound having the reactive hydrogen group.

[0013]

25 More specifically, according to the present invention, the negative charging toner, a developing agent, a container provided by filling the developing agent, an image forming method, and an image forming apparatus as described below are provided.

[1] Negative charging toner obtained by dissolving or dispersing  
30 a toner composition containing a toner binder resin including a modified polyester type resin (i) reactible with a compound having an active hydrogen group in an organic solvent to provide a dissolved product or a dispersed product, dispersing the

dissolved product or the dispersed product in an aqueous medium containing a resin fine particle, and simultaneously causing to react with the compound having the active hydrogen group, and removing the solvent from a thus obtained dispersing liquid,

5 wherein a storage modulus ( $G'$ ) of the toner at a frequency of 1 Hz and a temperature of 180 °C is 500 Pa or more.

[2] The negative charging toner as described in [1], in which the storage modulus ( $G'$ ) at the frequency of 1 Hz and the temperature of 180 °C is in a range of 700 to 7000 Pa.

10 [3] The negative charging toner as described in [1] or [2], in which the toner binder resin contains the modified polyester type resin (i) and a non-modified polyester type resin (ii), wherein a weight ratio of the modified polyester type resin (i) to the non-modified polyester type resin (ii) is in a range of 5/95 to  
15 75/25.

[4] The negative charging toner as described in any one of [1] to [3], in which an acid value of the toner binder resin is in a range of 0.5 to 40 mgKOH/g.

[5] The negative charging toner as described in any one of [1] through [4], in which a glass transition point ( $T_g$ ) of the toner binder resin is in a range of 40 to 70 °C.

[6] The negative charging toner as described in any one of [1] through [5], in which the resin fine particle includes any one of a vinyl type resin, a polyurethane resin, an epoxy resin and a  
25 polyester resin, or a mixture thereof.

[7] The negative charging toner as described in any one of [1] through [6], in which an average particle diameter of the resin fine particle is in a range of 5 to 500 nm.

[8] The negative charging toner as described in any one of [1] through [7], in which a volume average particle diameter of the toner particle is in a range of 4 to 8  $\mu\text{m}$ .

[9] The negative charging toner as described in any one of [1] through [8], in which a volume average particle diameter/number

average particle diameter ( $D_v/D_n$ ) of the toner particle is in a range of 1.10 to 1.25.

[10] The negative charging toner as described in any one of [1] through [9], in which an average degree of circularity of the toner particle is in a range of 0.90 to 0.96.

[11] The toner as described in any one of [1] through [10], in which a shape of the toner particle is a spindle shape.

[12] The negative charging toner as described in [11], in which the toner particle is in the spindle shape having a ratio ( $r_2/r_1$ ) of a short axis  $r_2$  to a long axis  $r_1$  of the toner particle is in a range of 0.5 to 0.8, and a ratio ( $r_3/r_2$ ) of thickness  $r_3$  to the short axis  $r_2$  of the toner particle is in a range of 0.7 to 1.0.

[13] The negative charging toner as described in any one of [1] through [12], in which the solvent is removed from an obtained dispersing liquid at least by agitating and/or heating the dispersing liquid.

[14] A developing agent including the negative charging toner as described in any one of [1] through [13].

[15] An image forming method using the developing agent as described in [14] in a developing device having a toner recycling mechanism.

[16] A container filled with the developing agent as described in [14].

[15] An image forming apparatus loaded with the container as described in [14].

[0014]

[Description of the Preferred Embodiments]

In the following, the present invention will be described in detail.

Negative charging toner according to the present invention is toner obtained by dissolving or dispersing a toner composition containing a toner binder resin including a modified polyester type resin (i) reactible with a compound having an active

hydrogen group in an organic solvent to provide a dissolved product or a dispersed product, dispersing the dissolved product or the dispersed product in an aqueous solvent containing a resin fine particle, and simultaneously causing to react with the compound having the active hydrogen group, and removing the solvent from an obtained dispersing liquid.

[0015]

According to the present invention, the dissolved product or the dispersed product is provided by dissolving or dispersing the toner composition containing the toner binder resin including the modified polyester type resin (i) reactible with the active hydrogen group in the organic solvent. The organic solvent usable therefor may be exemplified by the solvent inactive with polyisocyanate (3) or the like as described below such as an aromatic solvent (toluene, xylene, or the like), ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone, or the like), esters (ethyl acetate or the like), amides (dimethylformamide, dimethylacetamide, or the like) and ethers (tetrahydrofuran or the like).

[0016]

As the modified polyester type resin (i) reactible with the compound having the active hydrogen group, for example, a polyester prepolymer having an isocyanate group may be used. The polyester prepolymer (A) having the isocyanate group may be exemplified by a polycondensate of a polyol (1) and a polycarboxylic acid (2), and a product obtained by causing a polyester having the active hydrogen group to further react with the polyisocyanate (3). The active hydrogen group of the polyester may be exemplified by a hydroxyl group (alcoholic hydroxyl group and phenolic hydroxyl group), amino group, carboxyl group or mercapt group. The alcoholic hydroxyl group is preferable in particular.

[0017]



The polyol (1) may be exemplified by a diol (1-1) and a trihydric or higher polyol (1-2), and the diol (1-1) alone or a mixture of the diol (1-1) and a small amount of polyol (1-2) is preferable. The diol (1-1) may be exemplified by an alkylene glycol (ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-hexandiol, or the like); alkylene ether glycol (diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene ether glycol or the like); alicyclic diol (1,4-cyclohexane dimethanol, hydrogenated bisphenol A, or the like); bisphenols (bisphenol A, bisphenol F, bisphenol S, or the like); alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, or the like) adduct of the alicyclic diol; alkylene oxide (ethylene oxide, propylene oxide, butylene oxide, or the like) adduct of the bisphenols. The alkylene glycol having 2 to 12 carbon atoms and the alkylene oxide adduct of the bisphenols are preferable, and the alkylene oxide adduct of the bisphenols, and simultaneous use of the alkylene glycol having 2 to 12 carbon atoms therewith are particularly preferable.

[0018]

A trihydric or higher polycarboxylic acid (2-2) may be exemplified by an aromatic polycarboxylic acid having 9 to 20 carbon atoms (trimellitic acid, pyromellitic acid, or the like). In addition, the polycarboxylic acid (2) may be provided by causing to react with the polyol (1) using an anhydride of the acid as described above or a lower alkyl ester (methyl ester, ethyl ester, isopropyl ester, or the like).

[0019]

A ratio of the polyol (1) to the polycarboxylic acid (2) is normally in a range of 2/1 to 1/1, preferably 1.5/1 to 1/1, more preferably 1.3/1 to 1.02/1 as an equivalent ratio  $[OH]/[COOH]$  of the hydroxyl group  $[OH]$  to the carboxyl group  $[COOH]$ .

[0020]

The polyisocyanate (3) may be exemplified by an aliphatic polyisocyanate (tetramethylene diisocyanate, hexamethylene diisocyanate, 2,6-diisocyanate methylcaproate, or the like); alicyclic polyisocyanate (isophorone diisocyanate, cyclohexylmethane diisocyanate, or the like); aromatic diisocyanate (tolylene diisocyanate, diphenylmethane diisocyanate or the like); aromatic aliphatic diisocyanate ( $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl xylylene diisocyanate or the like); isocyanurates; blocking the polyisocyanate with a phenol derivative, oxime, caprolactam, or the like; and simultaneous use of two kinds or more thereof.

[0021]

A ratio of the polyisocyanate (3) is normally in a range of 5/1 to 1/1, preferably 4/1 to 1.2/1, more preferably 2.5/1 to 1.5/1 as an equivalent ratio  $[\text{NCO}]/[\text{OH}]$  of the isocyanate group  $[\text{NCO}]$  to the hydroxyl group  $[\text{OH}]$  of the polyester having the isocyanate group  $[\text{NCO}]$  and the hydroxyl group. When a ratio  $[\text{NCO}]/[\text{OH}]$  exceeds 5, a low-temperature fixing property is worsened. When a molar ratio of  $[\text{NCO}]$  is less than 1, a urea content in the modified polyester becomes low, and a hot offset proof property is worsened.

[0022]

A content of a polyisocyanate (3) constituent in the prepolymer (A) having the isocyanate group at an end is normally in a range of 0.5 to 40 wt%, preferably 1 to 30 wt%, more preferably 2 to 20 wt%. When the content is less than 0.5 wt%, the hot offset proof property is worsened to simultaneously become disadvantageous in respect of compatibility of a heat-resistant storage property and the low-temperature fixing property. Moreover, when the content exceeds 40 wt%, the low-temperature fixing property is worsened.

[0023]

A number of isocyanate group contained per molecule in the

prepolymer (A) having the isocyanate group is normally one or more, preferably 1.5 to 3 in average, more preferably 1.8 to 2.5 in average. When the number is less than one per molecule, a molecular weight of the modified polyester after a cross-linking reaction and/or an extension reaction becomes low, and the hot offset proof property is worsened.

[0024]

The trihydric or higher polyol (1-2) may be exemplified by a trihydric to octahydric or higher polyhydric aliphatic alcohol (glycerin, trimethylolethane, trimethylolpropane, pentaerythritol, sorbitol, or the like); trihydric or higher phenols (trisphenol PA, phenol novolak, cresol novolak, or the like); alkylene oxide adduct of the trihydric or higher polyphenols. The polycarboxylic acid (2) may be exemplified by a dicarboxylic acid (2-1) and the trihydric or higher polycarboxylic acid (2-2), and (2-1) alone and a mixture of (2-1) and a small amount of (2-2) are preferable. The dicarboxylic acid (2-1) may be exemplified by an alkylene dicarboxylic acid (succinic acid, adipic acid, sebacic acid or the like); alkenylene dicarboxylic acid (maleic acid, fumaric acid or the like); aromatic dicarboxylic acid (phthalic acid, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid. The alkenylene dicarboxylic acid having 4 to 20 carbon atoms and the aromatic dicarboxylic acid having 8 to 20 carbon atoms are preferable in particular.

[0025]

According to the present invention, the modified polyester type resin (i) may be used alone, and further a non-modified polyester type resin may be contained together with the resin (i) as a toner binder resin component. The resin (ii) is simultaneously used, and thus the low-temperature fixing property and gloss when used for a full color apparatus are improved.

[0026]

The polyester resin (ii) may be exemplified by a

polycondensate of a polyol (1) and a polycarboxylic acid (2) similar to a polyester component of the resin (i), and resin similar to the resin (i) is preferable. Moreover, the resin (ii) may be not only the non-modified polyester but also modified by a chemical bond other than a urea bond, for example, modified by a urethane bond. At least a part of the resins (i) and (ii) is preferably compatibilized in respect of the low-temperature fixing property and the hot offset proof property. Accordingly, the polyester component of the resin (i) and the polyester component of the resin (ii) have preferably a similar composition. A weight ratio of the resin (i) to the resin (ii) in a case of containing the resin (ii) is normally in a range of 5/95 to 75/25, preferably 10/90 to 25/75, more preferably 12/88 to 25/75, particularly preferably 12/88 to 22/78. When a weight ratio of the resin (i) is less than 5%, the hot offset proof property is worsened, and simultaneously it becomes disadvantageous in respect of the compatibility of the heat-resistant storage property and the low-temperature fixing property. Meanwhile, when a weight ratio of the resin (i) exceeds 75/25, a fixing lower limit temperature is increased, and fixing may not be performed in a low-temperature fixing system.

[0027]

A peak molecular weight of the resin (ii) is normally in a range of 1000 to 30000, preferably 1500 to 10000, more preferably 2000 to 8000. When the peak molecular weight is less than 1000, the heat-resistant storage property is worsened, and when the peak molecular weight exceeds 10000, the low-temperature fixing property is worsened. A hydroxyl value of the resin (ii) is preferably in a range of 5 or higher, more preferably 10 to 120, particularly preferably 20 to 80. When a value is less than 5, the toner becomes disadvantageous in respect of the compatibility of the heat-resistant storage property and the low-temperature fixing property.

[0028]

An acid value of the resin (ii) is normally in a range of 0.5 to 40, preferably 5 to 35. The acid value is provided, and thus a tendency of becoming a negative charge property is easily produced. Moreover, the resin exceeding the range for the acid value and the hydroxyl value, respectively, is easily affected by an environment of a high temperature and high humidity, and a low temperature and low humidity, and an image is easily deteriorated.

In addition, the acid value of the resin (i) is close to zero, and therefore the acid value of the toner binder resin is determined by the acid value of the resin (ii). Accordingly, when the acid value of the resin (ii) is in a range of 0.5 to 40, the acid value of the toner binder resin also becomes in a range of 0.5 to 40.

[0029]

According to the present invention, a glass transition point ( $T_g$ ) of the toner binder resin is normally in a range of 40 to 70 °C, preferably 45 to 65 °C. When the point is less than 40 °C, the heat-resistant storage property of the toner is worsened, and when the point exceeds 70 °C, the low-temperature fixing property becomes insufficient. When a urea modified polyester resin is caused to coexist, the toner according to the present invention shows a tendency that the heat-resistant storage property is favorable even if the glass transition point is low, as compared with publicly known polyester type toner.

[0030]

The modified polyester type resin (i) reactible with the compound having the active hydrogen group as used in the present invention may be manufactured according to a method as described below or the like.

The polyol (1) and the polycarboxylic acid (2) are heated at 150 to 280 °C in the presence of a publicly known esterification catalyst such as tetrabutoxy titanate and dibutyl

tin oxide, and water produced is distilled out under a reduced pressure, as needed, and thus the polyester having the hydroxyl group is obtained. Subsequently, the polyisocyanate (3) is caused to react with the polyester at 40 to 140 °C, and thus the

5 polyester prepolymer (A) having the isocyanate group is obtained. Furthermore, when using amines as a cross-linking agent and an extending agent, for example, the amines (B) are caused to react with the polyester prepolymer (A) at 0 to 140 °C, and thus the polyester modified with the urea bond is obtained. When causing  
10 the polyisocyanate (3) to react, and when causing (A) and (B) to react, a solvent may be also used, as needed. The usable solvent may be exemplified by a compound inactive with the polyisocyanate (3) such as an aromatic solvent (toluene, xylene or the like): ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone or  
15 the like): esters (ethyl acetate or the like): amides (dimethylformamide, dimethylacetamide, or the like) and ethers (tetrahydrofuran or the like).

[0031]

Moreover, when the non-modified polyester type resin (ii)  
20 is used simultaneously, the resin (ii) is manufactured according to a method similar to a method for the polyester having the hydroxyl group, to be dissolved and mixed in a solution after completing a reaction of the resin (i).

[0032]

25 Next, according to the present invention, the dissolved product or the dispersed product is dispersed in the aqueous medium containing the resin fine particle, and simultaneously to cause to react with the compound having the active hydrogen group.

The aqueous medium used for manufacturing the toner  
30 according to the present invention may be water alone, and a solvent mixable with water may be simultaneously used. The solvent mixable with water may be exemplified by an alcohol (methanol, isopropanol, ethylene glycol, or the like),

dimethylformamide, tetrahydrofuran, Cellosolves (methyl Cellosolve or the like) or lower ketones (acetone, methyl ethyl ketone, or the like).

[0033]

5 As the resin fine particle contained in the aqueous medium, any resin may be used if the resin may form an aqueous dispersing body. The resin fine particle may be a thermoplastic resin and a thermosetting resin as exemplified by a vinyl type resin, polyurethane resin, epoxy resin, polyester resin, polyamide resin, 10 polyimide resin, silicone type resin, phenol resin, melamine resin, urea resin, aniline resin, ionomer resin or polycarbonate resin. As the resin fine particle, two kinds or more of the resins may be simultaneously used. Among the resins, the vinyl type resin, polyurethane resin, epoxy resin or polyester resin, 15 and simultaneous use thereof are preferable because the aqueous dispersing body of a fine spherical resin particle may be easily obtained.

[0034]

The vinyl type resin may be a polymer obtained from 20 homopolymerization or copolymerization of a vinyl type monomer as exemplified by a styrene-(meth)acrylic ester copolymer, styrene butadiene copolymer, (meth)acrylic acid-acrylic ester copolymer, styrene-acrylonitrile copolymer, styrene-maleic anhydride copolymer or styrene-(meth)acrylic acid copolymer.

25 [0035]

An average particle diameter of the resin fine particle used according to the present invention is preferably in a range of 5 to 500 nm, particularly preferably 30 to 120nm. When the diameter is less than 5 nm, the resin is not emulsified to become 30 rice cake-like, and when the diameter is 500 nm, a particle diameter distribution at a time of emulsifying is broad, and a particle diameter distribution of the toner does not become sharp.

[0036]

According to the present invention, the dissolved product or the dispersed product is dispersed in the aqueous medium containing the resin fine particle, and simultaneously caused to react with the compound having the active hydrogen group.

5 Specifically, for example, the product may be obtained by forming by causing a dispersing body including the polyester prepolymer (A) having the isocyanate group or the like to react with the amines (B) or the like in the aqueous medium. A method for stably forming the dispersing body including the polyester prepolymer  
10 (A) or the like in the aqueous medium may be exemplified by adding a toner raw material composition including the polyester prepolymer (A) or the like into the aqueous medium to be dispersed by a shearing force. The polyester prepolymer (A) or the like, and another toner composition (hereinafter referred to  
15 also as a toner raw material) including a coloring agent, a coloring agent masterbatch, a releasing agent and a charge controlling agent, the non-modified polyester type resin (ii) or the like may be mixed when forming the dispersing body in the aqueous medium, more preferably, after mixing the toner raw  
20 material beforehand, a mixture thereof may be added and dispersed in the aqueous medium. Moreover, according to the present invention, another toner raw material such as the coloring agent, the releasing agent and the charge controlling agent may be not necessarily added when forming a particle in the aqueous medium,  
25 and may be added after forming the particle. For example, after forming a particle containing no coloring agent, the coloring agent may be added according to a publicly known dyeing method.

[0037]

Cross-linking and/or extension reaction time may be  
30 selected by reactivity according to a combination of an isocyanate group structure of the polyester prepolymer (A), the amines (B) and the like. The reaction time is normally in a range of 10 minutes to 40 hours, preferably 30 minutes to 12 hours. A



reaction temperature is normally in a range of 0 to 150 °C, preferably 15 to 45 °C. Moreover, a publicly known catalyst may be used, as needed. Specifically, dibutyl tin laurate, dioctyl tin laurate or the like may be exemplified. In particular, after  
5 emulsifying, the emulsified dispersing body is preferably ripened at 20 to 35 °C for 30 minutes to 6 hours while agitating.

[0038]

According to the present invention, the resin fine particle is contained in the aqueous medium because a toner particle  
10 diameter and distribution thereof are controlled by the resin fine particle. However, when the cross-linking reaction or the extension reaction is insufficient, the resin fine particle covers an uppermost surface of the toner. Therefore, even when performing washing later on, an unreacted compound having the  
15 active hydrogen group may easily remain near a toner surface as it is, and the residual compound having the active hydrogen group destabilizes charge control. In particular, when using the amines as the compound having the active hydrogen group for the polyester prepolymer (A) having the isocyanate group, and if the  
20 amines remain, the amines demonstrate a positive charge property, resulted in an unstable negative charge property. In order to prevent the problem, the polyester prepolymer having the isocyanate group is important to be sufficiently subjected to the cross-linking reaction and/or the extension reaction.

25 [0039]

According to the present invention, the amines may be used as the compound having the active hydrogen group. The amines (B) may be exemplified by a diamine (B1), trihydric or higher polyamine (B2), amino alcohol (B3), aminomercaptan (B4), amino  
30 acid (B5) or blocking (B6) the amino groups (B1) to (B5). The diamine (B1) may be exemplified by an aromatic diamine (phenylene diamine, diethyltoluene diamine, 4,4'-diaminodiphenyl methane, or the like); alicyclic diamine (4,4'-diamino-3,3'-dimethyl

dicyclohexyl methane, diamine cyclohexane, isophorone diamine, or the like); or aliphatic diamine (ethylene diamine, tetramethylene diamine, hexamethylene diamine, or the like).

[0040]

5       The trihydric or higher amine (B2) may be exemplified by a diethylene triamine or a triethylene tetramine. The amino alcohol (B3) may be exemplified by an ethanolamine or hydroxyethyl aniline. The aminomercaptan (B4) may be exemplified by an aminoethyl mercaptan or an aminopropyl mercaptan. The amino acid  
10   (B5) may be exemplified by an aminopropionic acid or an aminocaproic acid.

[0041]

      The blocking (B6) of the amino groups (B1) to (B5) may be exemplified by a ketimine compound obtained from the amines B1 to  
15   B5 and ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone or the like), and an oxazoline compound. Among the amines (B), (B1) and a mixture of (B1) and a small amount of (B2) are preferable.

[0042]

20       Furthermore, according to the cross-linking reaction and/or the extension reaction, the molecular weight of the modified polyester after finishing the reaction may be adjusted by using a terminator, as needed. The terminator may be exemplified by a monoamine (diethyl amine, dibutyl amine, butyl amine, lauryl  
25   amine or the like), or blocking them (ketimine compound).

[0043]

      A ratio of the amines (B) is normally in a range of 1/2 to 2/1, preferably 1.5/1 to 1/1.5, more preferably 1.2/1 to 1/1.2 as an equivalent ratio  $[NCO]/[NHx]$  of the isocyanate group  $[NCO]$  in  
30   the prepolymer (A) having the isocyanate group to an amino group  $[NHx]$  in the amines (B). When a ratio  $[NCO]/[NHx]$  is over 2 or less than 1/2, the molecular weight of an obtained urea modified polyester (i) becomes low, and the hot offset proof property is

worsened.

[0044]

An amount of using the aqueous medium relative to 100 parts by weight of the toner composition containing the modified polyester type resin (i) such as the polyester prepolymer (A) is normally in a range of 50 to 2000 parts by weight, preferably 100 to 1000 parts by weight. When the amount is less than 50 parts by weight, a dispersion state of the toner composition is poor and the toner particle having a predetermined particle diameter may not be obtained. The amount exceeding 20000 parts by weight is not economical. Moreover, a dispersing agent may be also used as needed. The dispersing agent is preferably used because a particle size distribution becomes sharp and simultaneously dispersion is stable.

15 [0045]

An amount of using the aqueous solvent relative to 100 parts by weight of the modified polyester type resin (i) such as the polyester prepolymer (A) is normally in a range of 0 to 300 parts by weight, preferably 0 to 100 parts by weight, more preferably 25 to 70 parts by weight. When the aqueous solvent is used, the aqueous solvent is removed by heating under normal pressure or reduced pressure after the extension reaction and/or the cross-linking reaction.

[0046]

25 According to the present invention, the dissolved product or the dispersed product is dispersed in the aqueous medium containing the resin fine particle. A method for dispersing the dissolved product or the dispersed product is not particular limited, and such a publicly known facility may be applied as a low-speed shearing type, a high-speed shearing type, a friction type, a high-pressure jet type and an ultrasonic wave. In order to provide the particle diameter of the dispersing body of 2 to 20  $\mu\text{m}$ , the high-speed shearing type is preferable. When a

high-speed shearing type disperser is used, a number of rotations has no particular limitation, and is normally in a range of 1000 to 30000 rpm, preferably 5000 to 20000 rpm. Dispersion time has no particular limitation, and in a case of a batch system, the time is normally in a range of 0.1 to 5 minutes. A temperature during dispersion is normally in a range of 0 to 150 °C (under pressure), preferably 40 to 98 °C. A high temperature is preferable because a viscosity of the dispersing body including the modified polyester type resin (i) or the like is low, and the dispersion is easy.

[0047]

According to the present invention, the dispersing agent for emulsifying and dispersing the dissolved product or the dispersed product (oily phase in which the toner composition is dispersed) in the aqueous medium containing the resin fine particle may be exemplified by an anionic surface active agent such as an alkylbenzene sulfonate, an  $\alpha$ -olefin sulfonate and a phosphoric acid ester, a cationic surface active agent such as an amine salt type including an alkylamine salt, an amino alcohol fatty acid derivative, a polyamine fatty acid derivative and an imidazoline, and a quarternary ammonium salt type such as an alkyl trimethyl ammonium salt, a dialkyl dimethylammonium salt, an alkyl dimethylbenzyl ammonium salt, a pyridinium salt, an alkyl isoquinolinium salt and a benzethonium chloride, a nonionic surface active agent such as a fatty acid amide derivative and a polyhydric alcohol derivative, and an amphoteric surface active agent such as an alanine, a dodecyl-di(aminoethyl)glycine, a di(octyl aminoethyl)glycine and an N-alkyl-N, N-dimethylammonium betaine.

[0048]

Moreover, a surface active agent having a fluoroalkyl group is used, and thus emulsifying and dispersing effect may be improved by using an extremely small amount. An anionic surface

active agent having the fluoroalkyl group preferably employed may be exemplified by a fluoroalkyl carboxylic acid having 2 to 10 carbon atoms and a metal salt thereof, perfluoro octanesulfonyl glutamic acid disodium,

5 3- $[\omega$ -fluoroalkyl(C6-C11)oxy]-1-alkyl(C3-C4)sodium sulfonate, 3- $[\omega$ -fluoroalkanoyl(C6-C8)-N-ethylamino]-1-sodium propanesulfonate, fluoroalkyl(C11-C20)carboxylic acid and metal salt thereof, perfluoroalkyl(C7-C13)carboxylic acid and metal salt thereof, perfluoroalkyl(C4-C12)sulfonic acid and metal salt  
10 thereof, perfluorooctane sulfonic acid diethanol amide, N-propyl-N-(2-hydroxyethyl)perfluoro octanesulfonamide, perfluoroalkyl(C6-C10)sulfonamide propyltrimethylammonium salt, perfluoroalkyl(C6-C10)-N-ethylsulfonyl glycine salt or mono-perfluoroalkyl(C6-C16)phosphoric acid ethylester. A trade  
15 name may be exemplified by Surflon S-111, S-112, S-113 (manufactured by Asahi Glass Co., Ltd.), Fluorad FC-93, FC95, FC-98, FC-129 (manufactured by Sumitomo 3M Co., Ltd.), Unidyne DS-101, DS-102, (manufactured by Daikin Industries, Ltd.), Megafac F-110, F-120, F-113, F-191, F-812, F-833 (manufactured by  
20 Dainippon Ink and Chemicals Inc.), Ektop EF-102, 103, 104, 105, 112, 123A, 123B, 306A, 501, 201 and 204 (manufactured by Tochem Products Co., Ltd.) or Ftergent F-100, F150 (manufactured by Neos Co., Ltd.).

[0049]

25 Moreover, the cationic surface active agent is preferably used as the dispersing agent. The cationic surface active agent may be exemplified by an aliphatic primary, secondary or tertiary amine acid having the fluoroalkyl group, aliphatic quarternary ammonium salt such as a perfluoroalkyl(C6-C10)sulfonamide  
30 propyltrimethylammonium salt, benzalkonium salt, benzethonium chloride, pyridinium salt or imidazolinium salt. A trade name may be exemplified by Surflon S-121 (manufactured by Asahi Glass Co., Ltd.), Fluorad FC-135 (manufactured by Sumitomo 3M Co., Ltd.),

Unidyne DS-202 (manufactured by Daikin Industries, Ltd.), Megafac F-150, F-824 (manufactured by Dainippon Ink and Chemicals Inc.), Ektop EF-132 (manufactured by Tochem products Co., Ltd.) or Ftergent F-300 (manufactured by Neos Co., Ltd.).

5 [0050]

Moreover, as an inorganic compound dispersing agent hardly soluble in water, a tricalcium phosphate, calcium carbonate, titanium oxide, colloidal silica, hydroxyapatite or the like may be also used.

10 [0051]

Moreover, a dispersing liquid drop may be stabilized by a polymer type protective colloid. For example, such a material may be used as a homopolymer or a copolymer of acids including an acrylic acid, methacrylic acid,  $\alpha$ -cyanoacrylic acid,

15  $\alpha$ -cyanomethacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid or maleic anhydride, or (meth)acrylic acid type monomer containing a hydroxyl group such as an acrylic acid

$\beta$ -hydroxyethyl, methacrylic acid  $\beta$ -hydroxyethyl, acrylic acid

$\beta$ -hydroxypropyl, methacrylic acid  $\beta$ -hydroxypropyl, acrylic acid

20  $\gamma$ -hydroxypropyl, methacrylic acid  $\gamma$ -hydroxypropyl,

acrylic acid-3-chloro-2-hydroxypropyl,

methacrylic acid-3-chloro-2-hydroxypropyl, diethylene glycol

monoacrylic acid ester, diethylene glycol monomethacrylic acid

ester, glycerol monoacrylic acid ester, glycerol monomethacrylic

25 acid ester, N-methylolacrylamide or N-methylolmethacrylamide,

vinyl alcohol or ethers with the vinyl alcohol including a

vinylmethyl ether, vinylethyl ether or vinyl propyl ether, esters

of a compound containing a vinyl alcohol and a carboxyl group

including a vinyl acetate, vinyl propionate or vinyl butyrate,

30 acrylamide, methacrylamide, diacetoneacrylamide or a methylol

compound thereof, acid chlorides including an acrylic acid

chloride or methacrylic acid chloride, having a nitrogen atom or

a heterocyclic ring including a vinylpyridine, vinylpyrrolidone,

vinylimidazole or ethyleneimine, polyoxyethylene type including a polyoxyethylene, polyoxypropylene, polyoxyethylene alkylamine, polyoxypropylene alkylamine, polyoxyethylene alkylamide, polyoxypropylene alkylamide, polyoxyethylene nonylphenyl ether, 5 polyoxyethylene lauryl phenyl ether, polyoxyethylene stearylphenyl ester or polyoxyethylene nonyl phenyl ester, and celluloses including a methyl cellulose, hydroxyethyl cellulose or hydroxypropylcellulose.

[0052]

10 In order to decrease viscosity of the toner composition to be obtained, a solvent in which the urea modified polyester and the polyester prepolymer (A) may be dissolved may be used. The solvent is preferably used because the particle size distribution becomes sharp. The solvent having volatility at a boiling point 15 less than 100 °C is preferable because the solvent may be easily removed. The solvent may be used alone or in combination with two kinds or more as exemplified by toluene, xylene, benzene, carbon tetrachloride, methylene chloride, 1,2-dichloroethane, 1,1,2-trichloroethane, trichloroethylene, chloroform, 20 monochlorobenzene, dichloroethylidene, methyl acetate, ethyl acetate, methyl ethyl ketone or methyl isobutyl ketone. In particular, an aromatic type solvent such as the toluene and the xylene, and a halogenated hydrocarbon such as the methylene chloride, the 1,2-dichloroethane, the chloroform, and the carbon 25 tetrachloride are preferable.

[0053]

The toner according to the present invention may be obtained by removing the solvent from a thus obtained dispersing liquid. In order to remove the solvent, such a method may be 30 adopted as gradually increasing a temperature of a whole system, and completely evaporating and removing the solvent in a liquid drop. Alternatively, the dispersing liquid is sprayed into a dry atmosphere to completely remove a non-aqueous organic solvent in

the liquid drop and to form a toner fine particle, and thus an aqueous dispersing agent may be simultaneously evaporated and removed. As the dry atmosphere to which the dispersing liquid is sprayed, such a gas is generally used as obtained by heating air, nitrogen, a carbon dioxide gas, combustion gas or the like, in particular, such various kinds of air currents are used as heated at a temperature equal to or higher than a boiling point of a maximum boiling point solvent used. Target quality may be sufficiently obtained from treatment in a short period of time by using a spray drier, a belt drier, a rotary kiln, or the like.

[0054]

According to the present invention, when the particle size distribution of the toner composition in the dispersing liquid is broad, and washing and drying treatment are performed while maintaining the particle size distribution, the particle size distribution may be adjusted by classifying to a desired particle size distribution.

A classification operation is performed by using a cyclone, decanter, centrifugal separation or the like in a liquid, and thus a fine particle part may be removed. It is obvious that the classification operation may be performed after acquiring the toner composition as a powder after drying, however, the operation is preferably performed in the liquid in respect of efficiency. A thus obtained undesired fine particle or coarse particle may be again returned to a kneading step, and may be used for forming the particle. In that case, the fine particle or the coarse particle may be used even in a wet state.

[0055]

The dispersing agent or the like is preferably removed from the obtained dispersing liquid as much as possible, to be preferably performed simultaneously with the classification operation as described above.

An obtained toner powder after drying may be mixed together



with a different kind of particles such as a releasing agent fine particle, a charge controlling fine particle, a fluidizing agent fine particle and a coloring agent fine particle, and elimination of different kind of particles from a surface of an obtained  
5 complex particle may be prevented by applying a mechanical impact force to a mixed power to be solidified and melted on the surface.

[0056]

A specific means may be exemplified by a method for applying impact force to a mixture by a blade rotating at high  
10 speed, and a method for charging the mixture to a current at high speed, accelerating, and causing particles to collide with each other or to collide the complex particle against an appropriate collision plate. A device may be exemplified by a device provided by decreasing a pulverizing air pressure through modifying  
15 Angmill (manufactured by Hosokawamicro Corp.) and I type mill (manufactured by Nippon Pneumatic Mfg. Co., Ltd.), a hybridization system (manufactured by Nara Machinery Co., Ltd.), Cryptron system (manufactured by Kawasaki Heavy Industries, Ltd.), or automatic mortar.

20 [0057]

According to the present invention, when removing the solvent from the obtained dispersing liquid, the solvent is preferably removed from the obtained dispersing liquid while ripening the cross-linking reaction and/or the extension reaction  
25 at least by agitating and/or heating the dispersing liquid.

[0058]

Thus, the modified polyester type resin reactible with the compound having the active hydrogen group is cross-linked or extended by using the compound having the active hydrogen group  
30 by agitating and/or heating to decrease an amount of the compound having the active hydrogen group in the toner particle, and toner having a storage modulus ( $G'$ ) in a specified range as described later may be easily obtained. According to the present invention,

in order to control the toner particle diameter and distribution thereof, the resin fine particle is contained in the aqueous medium. However, when the ripening as described above is insufficient, the cross-linking reaction and/or the extension reaction become insufficient, and the resin fine particle covers an uppermost surface of the toner particle. Therefore, even when applying the washing process later on, the unreacted compound having the active hydrogen group remains as it is, and the residual compound having the active hydrogen group may destabilize the charge control.

[0059]

The toner according to the present invention has the storage modulus ( $G'$ ) at a frequency of 1 Hz and a temperature of 180 °C in a range of 500 Pa or more, preferably 700 to 7000 Pa. When the storage modulus ( $G'$ ) is less than 500 Pa, an unreacted cross-linking agent or extending agent may remain, the negative charge property of the toner may be damaged, and an offset may be also produced. Meanwhile, when the  $G'$  exceeds 7000 Pa, if the toner according to the present invention is used in a device provided by adopting the low-temperature fixing system, the fixing lower limit temperature is increased, and rising time from waiting time may be lengthened.

[0060]

When the cross-linking reaction or the extension reaction is insufficient, the  $G'$  (storage modulus) of the toner at the frequency of 1 Hz and the temperature of 180 °C becomes 500 Pa or less, the unreacted cross-linking agent or extending agent remains to damage a toner negative charge property. Moreover, when the  $G'$  is 700 Pa or less, a hot offset is produced. Furthermore, when the  $G'$  is 7000 Pa or more, the fixing lower limit temperature is increased, and the rising time from the waiting time is lengthened according to Imagio Neo450 of our company provided by adopting the low-temperature fixing system.

[0061]

The toner is evaluated by the storage modulus ( $G'$ ) at the frequency of 1 Hz and the temperature of 180 °C in the present invention because the inventors of the present invention find  
5 that a progress of the cross-linking reaction and/or the extension reaction may be grasped by measuring the storage modulus ( $G'$ ), and that providing the storage modulus ( $G'$ ) to be 500 Pa or more is important to obtain the toner satisfying low-temperature fixing and having an excellent offset proof  
10 property. More specifically, a degree of polymerization or a degree of cross-linking of resin under synthesis is generally substituted by viscosity of the resin through measurement thereof during polymerization. However, a method for measuring the viscosity during polymerization is not appropriate in preparing  
15 the toner according to the present invention because a toner material other than a resin component is contained. Moreover, a measurement of the viscosity in a high temperature region approximately at 180 °C also may not be carried out in a toner preparation step. Accordingly, a degree of cross-linking reaction  
20 or extension reaction of the toner is found to be determined by an emulsifying condition and a ripening condition after emulsification, and the degree of cross-linking reaction or extension reaction is found to be evaluated in a certain range of viscoelasticity of the toner.

25 [0062]

The viscoelasticity of the toner according to the present invention is measured as described below. A measurement is performed by using ReoStress RS50 system manufactured by Haacke, using a parallel plate having a diameter of 20 mm and setting at  
30 the frequency of 1Hz, the temperature of 180 °C, and stress automatic. Toner provided in a pellet shape having a diameter of 20 mm and thickness of 2 mm is used.

[0063]

The toner according to the present invention preferably has a specific shape and a shape distribution. Specifically, an average degree of circularity is preferably in a range of 0.90 to 0.96, and such toner is effective to form a reproducible high quality image having proper density. The average degree of circularity is more preferably in a range of 0.940 to 0.955, and the particle having a degree of circularity less than 0.94 is preferably included by 15 % or less. When a degree of circularity exceeds 0.96, a cleaning failure is produced on a photoconductor, a transfer belt, or the like in a system provided by adopting blade cleaning or the like to cause stain on the image. For example, according to development and transfer at a low image area rate, an amount of transfer residual toner is small, and the problem of the cleaning failure is not posed. However, according to development and transfer at a high image area rate such as a color photograph image and further a sheet feeding failure or the like, untransferred toner subjected to image formation may be produced on the photoconductor as the transfer residual toner, and produce image background stain when the transfer residual toner accumulates. Moreover, the transfer residual toner contaminates a charge roller for providing a contact charge on the photoconductor, or the like, and incapacitate an original charge capability. Moreover, toner having a degree of circularity less than 0.90 and an amorphous shape too far from a spherical shape, a satisfactory transfer property and a high quality image without dust may not be obtained.

[0064]

As a method for metering the degree of circularity, such an optical detection zone technique is appropriate as passing a suspension containing the particle into an image pickup part detection zone on a flat plate, optically detecting and analyzing a particle image by using a CCD camera. A value obtained from the technique is such that a circumferential length of an equivalent

circle having an equal projection area is divided by a circumferential length of an actually existing particle. The obtained value is metered as the average degree of circularity by using a flow particle image analyzer FPIA-2100 (manufactured by TOA Medical Electronics Co., Ltd.). A specific measuring method will be described later.

[0065]

According to the toner of the present invention, a volume average particle diameter ( $D_v$ ) of the toner particle is preferably in a range of 4 to 8  $\mu\text{m}$ . In general, when a toner particle diameter is smaller, the toner particle diameter is believed to be more advantageous to obtain a high-definition and high quality image, however, to be reversely disadvantageous to a transfer property or a cleaning property. Moreover, when a volume average particle diameter ( $D_v$ ) is smaller than 4  $\mu\text{m}$ , the toner is melted and deposited on a carrier surface in agitation for a long time according to a developing device using a two-component developing agent, decreases a carrier charge capability, and use as one-component developing agent easily produces melting and depositing of the toner on a member such as a blade for thinning the toner.

[0066]

On the contrary, when a volume average particle diameter ( $D_v$ ) of the toner particle is larger than 8  $\mu\text{m}$ , the high-definition and high quality image becomes difficult to obtain, and simultaneously when the toner under development is balanced, a fluctuation of a toner particle diameter frequently becomes large.

[0067]

According to the toner of the present invention, a ratio of volume average particle diameter/number average particle diameter ( $D_v/D_n$ ) of the toner particle is preferably in a range of 1.10 to 1.25. When a ratio  $D_v/D_n$  exceeds 1.25, a high-definition and high

quality image becomes difficult to obtain, and simultaneously when the toner under development is balanced, a fluctuation of the toner particle diameter may frequently become large. On the other hand, when a ratio  $D_v/D_n$  is less than 1.10, a toner particle may be preferable from an aspect of stabilizing a toner behavior, uniformizing a charge quantity, however, the toner may not be sufficiently charged, and the cleaning property may be worsened.

[0068]

10 According to the toner of the present invention, a shape of the toner particle is preferably a spindle shape. When the toner has an amorphous shape, no definite shape, or a flat shape, powder flowability is poor, and thus following problems (1) to (3) are caused. That is, (1) a friction charge may not be smoothly performed, and therefore the problem of background stain is easily produced. (2) When developing a fine latent image dot, delicate and uniform toner arrangement is difficult to take, and dot reproducibility is inferior. (3) According to an electrostatic transfer system, the toner is difficult to be influenced by an electric line of force, and therefore transfer efficiency is inferior. Meanwhile, when the toner is close to a sphere, the powder flowability is too high to excessively act to external force, and therefore such a problem is posed that the toner particle is easily scattered outside the dot during developing and transferring. Moreover, spherical toner is easily rolled on a photoconductor, and therefore such a problem is posed that the toner particle submerges between the photoconductor and a cleaning member, which frequently produces the cleaning failure.

25 In addition, one example of the toner particle having the spindle shape is shown in Fig. 1 (a) and (b).

[0069]

To the contrary, the spindle-shaped toner according to the present invention is provided such that the powder flowability is

appropriately adjusted, and therefore the friction charge is smoothly performed to produce no background stain, the toner particle is developed in order relative to the fine latent image dot, and then efficiently transferred, excellent in dot reproducibility. Furthermore, relative to scattering at the time, the power flowability is appropriately braked and scattering is prevented. The spindle-shaped toner has a limited rolling axis, as compared with the spherical toner, and therefore the cleaning failure such as submerging below the cleaning member hardly occur.

[0070]

According to the toner of the present invention, the toner particle shape is preferably the spindle shape as described above. Specifically, the toner particle shape is preferably the spindle shape expressed by a ratio ( $r_2/r_1$ ) of a short axis  $r_2$  to a long axis  $r_1$  of the toner particle in a range of 0.5 to 0.8, and a ratio ( $r_3/r_2$ ) of thickness  $r_3$  to a length of the short axis  $r_2$  of the toner particle in a range of 0.7 to 1.0. When the toner particle shape is within such ranges, the shape is the spindle shape, and not the amorphous and the flat shape, and not the spherical shape, the shape satisfies all of a friction charge property, the dot reproducibility, the transfer efficiency, scattering prevention, the cleaning property of both shapes.

[0071]

In addition, the long axis  $r_1$ , the short axis  $r_2$ , and the thickness  $r_3$  of the toner particle refer to length defined as shown in Fig. 1 (b).

[0072]

When a ratio ( $r_2/r_1$ ) of the long axis  $r_1$  and the short axis  $r_2$  is less than 0.5, the toner particle shape is separated from the spherical shape, and therefore the cleaning property is high. However, the dot reproducibility and the transfer efficiency are inferior, and therefore the high-definition image quality may not be obtained. Moreover, when a ratio ( $r_3/r_2$ ) of the thickness  $r_3$  to

the short axis  $r_2$  is less than 0.7, the toner particle shape is close to the flat shape, and therefore scattering is small as indicated for the amorphous toner, but high efficiency as indicated for the spherical toner may not be obtained.

5 [0073]

Meanwhile, when a ratio ( $r_2/r_1$ ) of the long axis and the short axis exceeds 0.8, the toner particle shape comes close to the sphere, and therefore, the cleaning failure may occur in particular in the environment of a low temperature and low humidity. In particular, when a ratio ( $r_3/r_2$ ) of the thickness and the short axis is 1.0, a rotating body using the long axis as a rotating axis is provided.

[0074]

15 In addition, the long axis  $r_1$ , the short axis  $r_2$ , and the thickness  $r_3$  are measured by photographing and observing while changing an angle of a visual field by using a scanning electron microscope (SEM).

[0075]

20 As the coloring agent of the toner according to the present invention, all of publicly known dyes and pigments may be used as exemplified by a carbon black, Nigrosine dye, iron black, naphthol yellow S, Hanza yellow (10G, 5G, G), cadmium yellow, yellow iron oxide, ocher, chrome yellow, titanium yellow, polyazo yellow, oil yellow, Hanza yellow (GR, A, RN, R), pigment yellow L, benzidine yellow (G, GR), permanent yellow (NCG), Vulkan fast yellow (5G, R), tartrazine lake, quinoline yellow lake, anthrazane yellow BGL, isoindolinone yellow, red ocher, red lead, lead vermilion, cadmium red, cadmium mercury red, antimony vermilion, permanent red 4R, para red, fire red, 25 para-chloro-ortho-nitroaniline red, lithol fast scarlet G, brilliant fast scarlet, brilliant carmine BS, permanent red (F2R, F4R, FRL, FRii, F4RH), fast scarlet VD, Vulkan fast rubin B, brilliant scarlet G, lithol rubin GX, permanent red F5R, 30



brilliant carmine 6B, pigment scarlet 3B, Bordeaux 5B, toluidine maroon, permanent Bordeaux F2K, helio Bordeaux BL, Bordeaux 10B, Bon maroon light, Bon maroon medium, eosine lake, rohdamine lake B, rohdamine lake Y, alizarin lake, thioindigo red B, thioindigo maroon, oil red, quinacridone red, pyrazolone red, polyazo red, chromium vermillion, benzidine orange, perinone orange, oil orange, cobalt blue, cerulean blue, alkali blue lake, peacock blue lake, Victoria blue lake, non-metal phthalocyanine blue, phthalocyanine blue, fast sky blue, indanthrene blue (RS, BC), indigo, ultramarine, iron blue, anthraquinone blue, fast violet B, methyl violet lake, cobalt purple, manganese purple, dioxane violet, anthraquinone violet, chrome green, zinc green, chrome oxide, pyridian, emerald green, pigment green B, naphthol green B, green gold, acid green lake, malachite green lake, phthalocyanine green, anthraquinone green, titanium oxide, zinc white or lithopone, and a mixture thereof.

[0076]

A content of the coloring agent is normally in a range of 1 to 15 wt%, preferably 3 to 10 wt% relative the whole toner.

The coloring agent used according to the present invention may be also used as a masterbatch compounded with resin. Binder resin used for manufacturing the masterbatch, or kneaded with the masterbatch may be exemplified, in addition to the modified or non-modified polyester resin as exemplified above, by a polymer of styrene and substitution product thereof including polystyrene, poly-p-chlorostyrene, polyvinyl toluene or the like; a styrene type copolymer including a styrene-p-chlorostyrene copolymer, a styrene-propylene copolymer, a styrene-vinyltoluene copolymer, a styrene-vinylnaphthalene copolymer, a styrene-methylacrylate copolymer, a styrene-ethylacrylate copolymer, a styrene-butylacrylate copolymer, a styrene-octylacrylate a copolymer, styrene-methylmethacrylate copolymer, a styrene-ethylmethacrylate copolymer, a styrene-butylmethacrylate

copolymer, a styrene- $\alpha$ -chloromethylmethacrylate copolymer, a styrene-acrylonitrile copolymer, a styrene-vinylmethylketone copolymer, a styrene-butadiene copolymer, a styrene-isoprene copolymer, a styrene-acrylonitrile-indene copolymer, a  
5 styrene-maleic acid copolymer, a styrene-maleate copolymer, or the like; polymethylmethacrylate, polybutylmethacrylate, polyvinylchloride, polyvinylacetate, polyethylene, polypropylene, polyester, epoxy resin, epoxy polyol resin, polyurethane, polyamide, polyvinylbutyral, polyacrylic resin, rosin, modified  
10 rosin, terpene resin, aliphatic or alicyclic hydrocarbon resin, aromatic system petroleum resin, chlorinated paraffin or paraffin wax, and may be used alone or in mixing.

[0077]

The masterbatch may be obtained by mixing and kneading the  
15 resin and the coloring agent for the masterbatch through applying a high shearing force. In the case, the organic solvent may be used in order to improve an interaction between the coloring agent and the resin. Moreover, a so-called flushing method is also preferably used by mixing and kneading an aqueous paste  
20 containing coloring agent water with the resin and the organic solvent, moving the coloring agent to a resin side, and removing moisture and an organic solvent component because a wet cake of the coloring agent may be directly used without requiring drying. In order to perform mixing and kneading, a high shearing  
25 dispersion device such as a 3-roll mill is preferably used.

[0078]

Moreover, the toner according to the present invention may be also provided by containing wax together with the toner binder resin and the coloring agent. As the wax, publicly known wax may  
30 be used as exemplified by polyolefin wax (polyethylene wax, polypropylene wax, or the like); long chain hydrocarbon (paraffin wax, Sasol wax, or the like); carbonyl group-containing wax or the like. In particular, the carbonyl group-containing wax is

preferable. The carbonyl group-containing wax may be exemplified by a polyalkane acid ester (carnauba wax, montan wax, trimethylolpropane tribehenate, pentaerythritol tetrabehenate, pentaerythritol diacetate dibehenate, glycerine tribehenate, 5 1,18-octadecanediol distearate, or the like); polyalkanol ester (trimellitic acid tristearyl, distearyl maleate, or the like); polyalkane acid amide (ethylenediamine dibehenylamide or the like); polyalkylamide (trimellitic acid tristearylamide or the like); or dialkyl ketone (distearyl ketone or the like). Among 10 the carbonyl group-containing waxes, the polyalkane acid ester is preferable.

[0079]

A melting point of the above waxes is normally in a range of 40 to 160 °C, preferably 50 to 120 °C, more preferably 60 to 15 90 °C. Wax having a melting point less than 40 °C adversely affects the heat-resistant storage property, and wax having a melting point exceeding 160 °C easily produces a cold offset during fixing at a low temperature. Moreover, melt viscosity of the wax, as a measuring value at a temperature higher than the 20 melting point by 20 °C, is preferably in a range of 5 to 1000 cps, more preferably 10 to 100 cps. The wax having melt viscosity exceeding 1000 cps has poor improving effect on the hot offset proof property and the low-temperature fixing property. A content of the wax in the toner is normally in a range of 0 to 40 wt%, 25 preferably 3 to 30 wt%.

[0080]

The toner according to the present invention may be provided by containing a charge controlling agent as needed. All of publicly known agents may be used as the charge controlling 30 agent as exemplified by Nigrosine dye, triphenylmethane dye, chromium-containing metal complex dye, molybdic acid chelate pigment, rohdamine dye, alkoxy amine, a quarternary ammonium salt (including a fluorine modified quarternary ammonium salt),

alkylamide, a simple substance or a compound of phosphorus, a simple substance or a compound of tungsten, a fluorine type activating agent, a salicylic acid metal salt or a metal salt of salicylic acid derivative. Specifically, the charge controlling agent may be exemplified by Bontron 03 of the Nigrosine dye, Bontron P-51 of the quarternary ammonium salt, Bontron S-34 of the metal-containing azo dye, E-82 of the oxynaphthoic acid type metal complex, E-84 of the salicylic acid type metal complex or E-89 of the phenol-type condensate (manufactured by Orient Chemical Industries, Ltd.), TP-302, TP-415 of the quarternary ammonium salt molybdenum complex (manufactured by Hodogaya Chemical Co., Ltd.), Copy charge PSYVP2038 of the quarternary ammonium salt, Copy blue PR of the triphenylmethane derivative, Copy charge NEGVP2036 of the quarternary ammonium salt, Copy charge NXVP434 (manufactured by Hoechst A.G.), LRA901, LR-147 as a boron complex (manufactured by Japan Carlit Co., Ltd.), copper phthalocyanine, perylene, quinacridone, azo type pigment or other polymer type compound having a functional group including a sulfone group, a carboxyl group, a quarternary ammonium salt, or the like.

[0081]

An amount of using the charge controlling agent is determined by a toner manufacturing method including a kind of binder resin, presence or absence of an additive used as needed and a dispersion method, and not limited primarily, and preferably in a range of 0.1 to 10 parts by weight relative to 100 parts by weight of the binder resin, more preferably 0.2 to 5 parts by weight. When the amount exceeds 10 parts by weight, the toner charge is too high to reduce effect of a main charge controlling agent, an electrostatic attraction force with a development roller is increased to cause a decrease in flowability of the developing agent, and a decrease in image density. The charge controlling agents may be dissolved and

dispersed after being melted and kneaded with the masterbatch, directly added when being melted and dispersed in the organic solvent, or solidified after forming the particle on the toner surface.

5 [0082]

The toner according to the present invention is preferably produced by adding an external additive in order to assist flowability, a development property, or a charge property of a coloring particle obtained according to the present invention. As  
10 the external additive, an inorganic fine particle may be preferably used. A primary particle diameter of the inorganic fine particle is preferably in a range of 5 m $\mu$  to 2  $\mu$ m, particularly 5 m $\mu$  to 500 m $\mu$ . Moreover, a specific surface area by BET method is preferably in a range of 20 to 500 m<sup>2</sup>/g. A ratio  
15 of using the inorganic fine particle is preferably in a range of 0.01 to 5 wt%, particularly preferably 0.01 to 2.0 wt% relative to the toner.

[0083]

The inorganic fine particle may be specifically exemplified  
20 by a silica, alumina, titanium oxide, barium titanate, magnesium titanate, calcium titanate, strontium titanate, zinc oxide, tin oxide, quartz sand, clay, mica, wollastonite, diatom earth, chrome oxide, cerium oxide, red iron oxide, antimony trioxide, magnesium oxide, zirconium oxide, barium sulfate, barium carbonate, calcium  
25 carbonate, silicon carbide, silicon nitride, or the like.

[0084]

In addition, the external additive may be exemplified by a polymer type fine particle including a polystyrene or methacrylate or acrylate copolymer obtained according to a  
30 soap-free emulsion polymerization, suspension polymerization and dispersion polymerization, or a polymer particle due to polycondensation type such as a silicone and a benzoguanamine and a nylon, or a thermosetting resin.

[0085]

The external additive such as a fluidizing agent is provided by performing a surface treatment to improve hydrophobicity, and worsening of a flow characteristic or a charge characteristic may be prevented even under high humidity. A preferable surface treatment agent may be exemplified by a silane coupling agent, a sililating agent, a silane coupling agent having a fluoroalkyl group, an organic titanate type coupling agent, an aluminum type coupling agent, silicone oil, modified silicone oil, or the like.

A cleaning improving agent for removing a residual developing agent after transfer on the photoconductor or a primary transfer medium may be used, as exemplified by a fatty acid metal salt including a zinc stearate, calcium stearate, stearic acid or the like, a polymer fine particle manufactured according to a soap-free emulsion polymerization or the like including a polymethyl methacrylate fine particle, polystyrene fine particle, or the like. The polymer fine particle has preferably a relatively narrow particle size distribution and the volume average particle diameter in a range of 0.01 to 1  $\mu\text{m}$ .

[0086]

When using the toner according to the present invention for the two-component developing agent, the toner may be used by mixing with a magnetic carrier, and a ratio of containing the carrier and the toner in the developing agent is preferably in a range of 1 to 10 parts by weight of the toner relative to 100 parts by weight of the carrier. As the magnetic carrier, such a conventionally publicly known carrier may be used as an iron powder, a ferrite powder, a magnetite powder and a magnetic resin carrier having approximately 20 to 200  $\mu\text{m}$  in particle diameter.

[0087]

Moreover, a coating material may be exemplified by an amino resin, urea-formaldehyde resin, melamine resin, benzoguanamine

resin, urea resin, polyamide resin, or epoxy resin. Moreover, the resin may be used as exemplified by a polyvinyl type resin and a polyvinylidene type resin including an acrylic resin, polymethyl methacrylate resin, polyacrylonitrile resin, polyvinylacetate resin, polyvinyl alcohol resin, polyvinylbutyral resin, polystyrene type resin such as a polystyrene resin and a styrene acrylic copolymer resin, halogenated olefin resin such as a polyvinylchloride, polyester type resin such as a polyethylene terephthalate resin and a polybutyrene terephthalate resin, polycarbonate type resin, polyethylene resin, polyvinylfluoride resin, polyvinylidenefluoride resin, polytrifluoroethylene resin, polyhexafluoropropylene resin, a copolymer of fluorovinylidene and an acryl monomer, a copolymer of fluorovinylidene and vinyl fluoride, fluoroterpolymer such as a terpolymer of tetrafluoroethene, fluorovinylidene and non-fluorized monomer, or silicone resin.

[0088]

Moreover, an electroconductive powder or the like may be contained in the coating material as needed. As the electroconductive powder, such a powder may be used as exemplified by a metal powder, carbon black, titanium oxide, tin oxide or zinc oxide. The electroconductive powder has preferably an average particle diameter of 1  $\mu\text{m}$  or less. When the average particle diameter becomes larger than 1  $\mu\text{m}$ , control of an electric resistance becomes difficult.

[0089]

Moreover, the toner according to the present invention may be also used as one-component magnetic toner without using the carrier or non-magnetic toner.

[0090]

[Embodiment]

In the following, the present invention will be further described by using examples. However, the present invention is

not limited thereto. Moreover, a part in the examples and comparative examples represents a part by weight.

[0091]

[Example 1]

5 (1) Preparation of resin fine particle dispersing liquid

Into a reaction vessel with a stirrer and a thermometer, 683 parts of water, 15 parts of sodium salt of methacrylic acid-ethylene oxide adduct sulfuric acid ester (Eleminol RS-30, manufactured by Sanyo Chemical Industries, Ltd.), 83 parts of  
10 styrene, 83 parts of methacrylic acid, 110 parts of butyl acrylate, 1 part of ammonium persulfate are charged, and agitated at 400 revolutions/minute for 15 minutes, and thus a white emulsion is obtained. A temperature in a system is increased up to 75 °C by heating to be allowed to react for 5 hours.

15 Furthermore, 30 parts of 1 % ammonium persulfate aqueous solution are added, ripened at 75 °C for 5 hours, and thus an aqueous dispersing liquid [Resin fine particle dispersing liquid 1] of vinyl type resin (copolymer of sodium salt of styrene-methacrylic acid-butyl acrylate-methacrylic acid-ethylene oxide adduct  
20 sulfuric acid ester) is obtained. A weight average particle diameter obtained by measuring the [Resin fine particle dispersing liquid 1] by LA-920 is 60 nm. A part of [Resin fine particle dispersing liquid 1] is dried, and a resin portion is separated.

25 [0092]

(2) Preparation of aqueous medium

After 990 parts of water, 83 parts of [Resin fine particle dispersing liquid 1], 37 parts of 48.5 % aqueous solution of sodium dodecyl diphenyl ether disulfonate (Eleminol MON-7:  
30 manufactured by Sanyo Chemical Industries, Ltd.), and 90 parts of ethyl acetate are mixed and agitated, a milky liquid is obtained. The obtained liquid is represented as [Aqueous phase 1].

[0093]



### (3) Synthesis of low molecule polyester 1

Into a reaction vessel with a cooling tube, a stirrer, and a nitrogen induction tube, 229 parts of bisphenol A-ethylene oxide 2 mole adduct, 529 parts of bisphenol A-propylene oxide 3 mole adduct, 208 parts of terephthalic acid, 46 parts of adipic acid, and 2 parts of dibutyl tin oxide are introduced, allowed to react at 230 °C for 8 hours under normal pressure, and further for 5 hours under a reduced pressure of 10 to 15 mmHg, and then 44 parts of trimellitic acid anhydride are introduced into the reaction vessel, allowed to react at 180 °C for 2 hours under normal pressure, and thus [Low molecule polyester 1] is obtained as a non-modified polyester type resin (ii). The [Low molecule polyester 1] has a number average molecular weight of 2500, a weight average molecular weight of 6700, Tg of 43 °C, and an acid value of 25.

[0094]

### (4) Synthesis of intermediate polyester and prepolymer

Into a reaction vessel with a cooling tube, a stirrer and a nitrogen induction tube, 682 parts of bisphenol A-ethylene oxide 2 mole adduct, 81 parts of bisphenol A-propylene oxide 2 mole adduct, 283 parts of terephthalic acid, 22 parts of trimellitic acid anhydride, and 2 parts of dibutyl tin oxide are introduced, allowed to react at 230 °C for 8 hours under normal pressure, and further for 5 hours under a reduced pressure of 10 to 15 mmHg, and thus [Intermediate polyester 1] is obtained.

The [Intermediate polyester 1] has a number average molecular weight of 2100, a weight average molecular weight of 9500, Tg of 55 °C, an acid value of 0.5, and a hydroxyl value of 51.

Next, into a reaction vessel with a cooling tube, a stirrer and a nitrogen induction tube, 410 parts of [Intermediate polyester 1], 89 parts of isophorone diisocyanate, and 500 parts of ethyl acetate are introduced, allowed to react at 100 °C for 5

hours, and thus [Prepolymer 1] is obtained as a modified polyester type resin (i) reactible with a compound having an active hydrogen group. A free isocyanate wt% in [Prepolymer 1] is 1.53 %.

5 [0095]

(5) Synthesis of ketimine

Into a reaction vessel with a stirrer and a thermometer, 170 parts of isophorone diamine and 75 parts of methyl ethyl ketone are charged, allowed to react at 50 °C for 5 hours, and  
10 thus [Ketimine compound 1] is obtained as a compound having an active hydrogen group. An amine value of [Ketimine compound 1] is 418.

[0096]

(6) Synthesis of masterbatch

15 After 1200 parts of water, 800 parts of carbon black (Printex35, manufactured Degusa AG) [DBP oil absorption = 42 ml/100 mg, pH = 9.5], and 1200 parts of polyester resin are added, and mixed by using a Henschel mixer (manufactured by Mitsui Mining Co., Ltd.), a mixture is kneaded at 150 °C for 30 minutes  
20 by using two rolls, and then rolled, cooled and pulverized by using a pulverizer, and thus [Masterbatch 1] is obtained.

[0097]

(7) Preparation of oil phase in which toner composition is dispersed

25 Into a vessel with a stirrer and a thermometer, 378 parts of [Low molecule polyester 1], 110 parts of carnauba wax, 22 parts of CCA (salicylic acid metal complex E-84: Orient Chemical Industries, Ltd.), and 947 parts of ethyl acetate are charged, subjected to a temperature increase at 80 °C under agitation,  
30 maintained at 80 °C for 5 hours, and then cooled to 30 °C in one hour. Next, into the vessel, 500 parts of [Masterbatch 1], and 500 parts of ethyl acetate are charged, mixed for one hour, and thus [Raw material dissolving liquid 1] is obtained.

After moving 1324 parts of [Raw material dissolving liquid 1] into a vessel, carbon black and wax are dispersed at liquid feeding velocity of 1 kg/hr, at disc peripheral velocity of 6 m/second through filling 5 mm zirconia beads by 80 volume % under a condition of three paths using a beads mill (Ultraviscomill, manufactured by Aimex Co., Ltd.). Next, 1324 parts of 65 % ethyl acetate solution of [low molecule polyester 1] are added, subjected to one path using the beads mill under the condition as described above, and thus [Pigment and wax dispersing liquid 1] is obtained. A solid concentration of [Pigment and wax dispersing liquid 1] (130 °C, 30 minutes) is 50 %.

[Toner 1] is obtained by using each material as described above by the operation means as described below.

[0098]

(8) Emulsifying => Ripening (cross-linking agent reaction and/or extension reaction in aqueous medium) => Solvent removal

Into a vessel, 749 parts of [Pigment and wax dispersing liquid 1], 115 parts of [Prepolymer 1], and 2.9 parts of [Ketimine compound 1] are introduced, mixed at 5,000 rpm for one minute by using TH Homo Mixer (manufactured by Tokushu Kika Kogyo Co., Ltd.), and then 1200 parts of [Aqueous phase 1] are added into the vessel, mixed at revolutions of 13,000 rpm for 20 minutes by using the TK Homo Mixer, and thus [Emulsifying slurry 1] is obtained.

Into a vessel with a stirrer having a paddle-type blade and a thermometer, the [Emulsifying slurry 1] is charged, ripened under conditions of 200 rpm and 28 °C for 90 minutes, next, solvent removal is performed at 30 °C for 8 hours, and then [Dispersing slurry 1] is obtained. The [Dispersing slurry 1] has a volume average particle diameter of 6.01  $\mu\text{m}$ , and a number average particle diameter of 5.75  $\mu\text{m}$  (measured by Multisizer II).

[0099]

(9) Washing => Drying

After filtering 100 parts of [Dispersing slurry 1] under reduced pressure:

①: Into a filter cake, 100 parts of ion exchange water are added, mixed (at revolutions of 12,000 rpm for 10 minutes) by using TK  
5 Homo Mixer, and then filtered.

②: Into a filter cake of ①, 100 parts of 10 % hydrochloric acid are added, mixed (at revolutions of 12,000 rpm for 10 minutes) by using the TK Homo Mixer, and then filtered.

③: Into a filter cake of ②, 300 parts of ion exchange water at  
10 25 °C are added, mixed (at revolutions of 12,000 rpm for 10 minutes) by using the TK Homo Mixer, and then a filtering operation is performed two times, and thus [Filter cake 1] is obtained.

The [Filter cake 1] is dried at 45 °C for 48 hours by using  
15 an air-circulating drier, sieved by using a mesh having an opening of 75  $\mu\text{m}$ , and thus the [Toner 1] is obtained.

[0100]

[Example 2]

(1) Emulsifying => Ripening (cross-linking agent reaction and/or  
20 extension reaction in aqueous medium) => Solvent removal

Similar to example 1, into a vessel with a stirrer having a paddle-type blade and a thermometer, the [Emulsifying slurry 1] is charged, ripened under conditions of 200 rpm and 32 °C for 30 minutes, next, solvent removal is performed at 30 °C for 8 hours,  
25 and then [Dispersing slurry 2] is obtained. The [Dispersing slurry 2] has a volume average particle diameter of 5.56  $\mu\text{m}$ , and a number average particle diameter of 5.19  $\mu\text{m}$  (measured by Multisizer II).

[0101]

30 (2) Washing => Drying

Similar to example 1, washing, filtering and drying are performed, and thus [Filter cake 2] is obtained.

The [Filter cake 2] is dried at 45 °C for 48 hours by using the air-circulating drier, sieved by using the mesh having the opening of 75  $\mu\text{m}$ , and thus [Toner 2] is obtained.

[0102]

5 [Example 3]

(1) Emulsifying => Ripening (cross-linking agent reaction and/or extension reaction in aqueous medium) => Solvent removal

Similar to example 1, into a vessel with a stirrer having a paddle-type blade and a thermometer, the [Emulsifying slurry 1]  
10 is charged, ripened under conditions of 180 rpm and 25 °C for 4 hours, next, solvent removal is performed at 30 °C for 8 hours, and then [Dispersing slurry 3] is obtained. The [Dispersing slurry 3] has a volume average particle diameter of 6.22  $\mu\text{m}$ , and a number average particle diameter of 5.90  $\mu\text{m}$  (measured by  
15 Multisizer II).

[0103]

(2) Washing => Drying

Similar to example 1, washing, filtering and drying are performed, and thus [Filter cake 3] is obtained.

20 The [Filter cake 3] is dried at 45 °C for 48 hours by using the air-circulating drier, sieved by using the mesh having the opening of 75  $\mu\text{m}$ , and thus [Toner 3] is obtained.

[0104]

[Example 4]

25 Similar to example 1, into a vessel with a stirrer having a paddle-type blade and a thermometer, the [Emulsifying slurry 1] is charged, ripened under conditions of 180 rpm and 27 °C for 2 hours, next, solvent removal is performed at 30 °C for 8 hours, and then [Dispersing slurry 4] is obtained. The [Dispersing  
30 slurry 4] has a volume average particle diameter of 6.48  $\mu\text{m}$ , and a number average particle diameter of 5.77  $\mu\text{m}$  (measured by Multisizer II).

[0105]

(2) Washing => Drying

In a manner similar as Example 1, washing, filtering and drying are performed, and thus [Filter cake 4] is obtained.

5       The [Filter cake 4] is dried at 45 °C for 48 hours by using the air-circulating drier, sieved by using the mesh having the opening of 75  $\mu$ m, and thus [Toner 4] is obtained.

[0106]

[Example 5]

10       Into a vessel, 753 parts of [Pigment and wax dispersing liquid 1], 154 parts of [Prepolymer 1] and 3.8 parts of [Ketimine compound 1] are introduced, mixed at 5,000 rpm for one minute by using TH Homo Mixer (manufactured by Tokushu Kika Kogyo Co., Ltd.), and then 1200 parts of [Aqueous phase 1] is added into the  
15       vessel, mixed at revolutions of 13,000 rpm for 20 minutes by using the TK Homo Mixer, and thus [Emulsifying slurry 2] is obtained. [Toner 5] is obtained similar to example 1 except for using the [Emulsifying slurry 2] instead of the [Emulsifying slurry 1] in example 1.

20       [0107]

[Example 6]

(3) Synthesis of low molecule polyester 1

      Into a reaction vessel with a cooling tube, a stirrer and a nitrogen induction tube, 196 parts of bisphenol A-propylene oxide  
25       2 mole adduct, 553 parts of bisphenol A-ethylene oxide 2 mole adduct, 210 parts of terephthalic acid, 79 parts of adipic acid and 2 parts of dibutyl tin oxide are introduced, allowed to react at 230 °C for 8 hours under normal pressure, and further for 5  
      hours under reduced pressure of 10 to 15 mmHg, and then 26 parts  
30       of trimellitic acid anhydride are introduced into the reaction vessel, allowed to react at 180 °C for 2 hours under normal pressure, and thus [Low molecule polyester 2] is obtained. The [Low molecule polyester 2] has a number average molecular weight

of 2400, a weight average molecular weight of 6200, Tg of 43 °C, and an acid value of 15.

[0108]

(2) [Emulsifying slurry 3] is obtained similar to example 1 except for using the [Low molecule polyester 2] instead of the [Low molecular polyester 1] in example 1, and [Toner 6] is obtained similar to example 1 except that the [Emulsifying slurry 3] is charged into the vessel with a stirrer having a paddle-type blade and a thermometer, ripened under conditions of 230 rpm and 25 °C for 75 hours, and then solvent removal is performed at 30 °C for 8 hours.

[0109]

[Example 7]

Similar to example 6, into the vessel with a stirrer having the paddle-type blade and a thermometer, the [Emulsifying slurry 3] is charged, ripened under conditions of 230 rpm and 28 °C for 60 minutes, next, solvent removal is performed at 30 °C for 8 hours, and then [Dispersing slurry 7] is obtained. The [Dispersing slurry 7] has a volume average particle diameter of 6.67  $\mu\text{m}$ , and a number average particle diameter of 5.47  $\mu\text{m}$  (measured by Multisizer II).

[0110]

(2) Washing => Drying

Similar to example 1, washing, filtering and drying are performed, and thus [Filter cake 7] is obtained.

The [Filter cake 7] is dried at 45 °C for 48 hours by using the air-circulating drier, sieved by using the mesh having the opening of 75  $\mu\text{m}$ , and thus [Toner 7] is obtained.

[0111]

[Comparative example 1]

After charging 451 g of 0.1 M- $\text{Na}_3\text{PO}_4$  aqueous solution into 709 g of ion exchange water, a mixture is heated at 60 °C, and

agitated at 12,000 rpm by using TK Homo Mixer. After gradually adding 68 g of 1.0 M- $\text{CaCl}_2$  aqueous solution into the solution, an aqueous medium containing  $\text{Ca}_3(\text{PO}_4)_2$  is obtained. After charging 170 g of styrene, 30 g of 2-ethylhexylacrylate, 10 g of Regal 400R, 60 g of paraffin wax (s. p. 70 °C), 5g of di-tert-butyl salicylic acid metallic compound, 10g of styrene-methacrylic acid copolymer (Mw 50,000, an acid value 20 mgKOH/g) into the TK Homo Mixer, a mixture is heated at 60 °C, and uniformly dissolved and dispersed at 12,000rpm. Into the mixture, 10 g of polymerization initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) is dissolved, and thus a polymeric monomer system is prepared. Into the aqueous medium, the polymeric monomer system is charged, agitated at 60 °C in a nitrogen atmosphere at 10,000 rpm for 20 minutes by using the TK Homo Mixer, and thus the polymeric monomer system is granulated. Then, a mixture is allowed to react at 60 °C for 3 hours while agitating by using a paddle agitating blade, a liquid temperature is provided at 80 °C, and allowed to react for 10 hours. After terminating a polymerization reaction, a reaction mixture is cooled, hydrochloric acid is added to dissolve calcium phosphate, and then filtration, water washing and drying are performed, and thus [Toner 8] is obtained.

[0112]

[Comparative example 2]

(1) Preparation of wax particle aqueous dispersing liquid 1

Into a 1000 ml 4-head flask provided by attaching an agitating device, a temperature sensor, a nitrogen introduction tube and a cooling tube, 28.5 g of Newcol 565C (manufactured by Nippon Nyukazai Co., Ltd) and 185.5 g of Carnauba Wax No. 1 (manufactured by Noda Wax Co., Ltd.) are added into 500 ml of deaerated distilled water, and a temperature is increased while agitating under a nitrogen gas flow. After adding 5N sodium hydroxide aqueous solution at an internal temperature of 85 °C and



increasing a temperature up to 75 °C in situ, heating and agitation are continued in situ for 1 hour, and cooling is performed to room temperature, and thus [Wax particle aqueous dispersing liquid 1] is obtained.

5 [0113]

(2) Preparation of coloring agent aqueous dispersing liquid 1

After 100 g of carbon black (trade name: Mogal L, manufactured by Cabot Corp.) and 25 g of sodium dodecyl sulfate are added into 540 ml of distilled water and sufficiently  
10 agitated, [Coloring agent dispersing liquid 1] is obtained by performing dispersion by using a pressurizing dispersing device (MINI-LAB: manufactured by Raney Inc.).

[0114]

(3) Synthesis of binder fine particle aqueous dispersing liquid

15 Into a 1L 4-head flask with an agitating device, a cooling tube, a temperature sensor, and a nitrogen introduction tube, 480 g of distilled water, 0.6 g of sodium dodecyl sulfate, 106.4 g of styrene, 43.2 g of n-butylacrylate and 10.4 g of methacrylic acid are added, and temperature is increased up to 70 °C under a  
20 nitrogen gas flow while agitating. After adding an initiator aqueous solution provided by dissolving 2.1 g of potassium persulfate into 120 ml of distilled water, performing agitation at 70 °C for 3 hours under a nitrogen gas flow, and completing polymerization, a reaction mixture is cooled at room temperature,  
25 and thus [High molecular weight binder resin fine particle dispersing liquid 1] is obtained.

[0115]

Into a 5L 4-head flask with an agitating device, a cooling tube, a temperature sensor, and a nitrogen introduction tube,  
30 2400 g of distilled water, 2.8 g of sodium dodecyl sulfate, 620 g of styrene, 128 g of n-butylacrylate, 52 g of methacrylic acid and 27.4 g of tert-dodecyl mercaptan are added, and temperature is increased up to 70 °C under a nitrogen gas flow while agitating.

After adding an initiator aqueous solution provided by dissolving 11.2 g of potassium persulfate into 600 ml of distilled water, performing agitation at 70 °C for 3 hours under a nitrogen gas flow, and completing polymerization, a reaction mixture is cooled at room temperature, and thus [Low molecular weight binder resin fine particle dispersing liquid 2] is obtained.

[Toner 9] is obtained by using each material as described above according to an operation means as described below.

[0116]

#### 10 (4) Synthesis of toner

Into a 1L separable flask provided with an agitating device, a cooling tube and a temperature sensor, 47.6 g of [High molecular weight binder fine particle dispersing liquid 1], 190.5 g of [Low molecular weight binder fine particle dispersing liquid 2], 7.7 g of [Wax particle aqueous dispersing liquid 1], 26.7 g of [Coloring agent dispersing liquid 1] and 252.5 ml of distilled water are mixed and agitated, and then an adjustment is performed at pH = 9.5 by using a 5 N-sodium hydroxide aqueous solution. Furthermore, under agitation, a sodium chloride aqueous solution provided by dissolving 50 g of sodium chloride and 600 ml of distilled water, 77 ml of isopropanol, and a surface active agent aqueous solution provided by dissolving 10 mg of Fluorad FC-170C (manufactured by Sumitomo 3 M Co., Ltd.: fluorine type nonionic surface active agent) in 10 ml of distilled water are sequentially added, allowed to react by increasing an internal temperature up to 85 °C for 6 hours, and then cooled to a room temperature. This reaction liquid is adjusted at pH = 13 by using the 5 N-sodium hydroxide aqueous solution, and then filtration is performed, re-suspension is further performed into distilled water, filtration and re-suspension are repeated, washing is performed, and then drying is performed, and thus the [Toner 9] is obtained.

[0117]

[Comparative example 3]

(1) Emulsifying => Ripening (cross-linking agent reaction and/or extension reaction in aqueous medium) => Solvent removal

Similar to example 1, into a vessel with a stirrer having a paddle-type blade and a thermometer, the [Emulsifying slurry 1] is charged, ripened under conditions of 200 rpm and 15 °C for 15 minutes, next, solvent removal is performed at 30 °C for 8 hours, and then [Dispersing slurry 10] is obtained. The [Dispersing slurry 10] has a volume average particle diameter of 5.22  $\mu\text{m}$ , and a number average particle diameter of 4.54  $\mu\text{m}$  (measured by Multisizer II).

[0118]

2) Washing => Drying

Similar to example 1, washing, filtering and drying are performed, and thus [Filter cake 10] is obtained.

The [Filter cake 10] is dried at 45 °C for 48 hours by using an air-circulating drier, sieved by using a mesh having an opening of 75  $\mu\text{m}$ , and thus [Toner 10] is obtained.

[0119]

[Comparative example 4]

(1) Emulsifying => Ripening (cross-linking agent reaction and/or extension reaction in aqueous medium) => Solvent removal

Similar to example 6, into a vessel with a stirrer having a paddle-type blade and a thermometer, the [Emulsifying slurry 3] is charged, ripened under conditions of 230 rpm and 33 °C for 12 hours, next, solvent removal is performed at 30 °C for 8 hours, and then [Dispersing slurry 7] is obtained. The [Dispersing slurry 7] has a volume average particle diameter of 7.84  $\mu\text{m}$ , and a number average particle diameter of 6.03  $\mu\text{m}$  (measured by Multisizer II).

[0120]

2) Washing => Drying

Similar to example 1, washing, filtering and drying are performed, and thus [Filter cake 11] is obtained.

The [Filter cake 11] is dried at 45 °C for 48 hours by using an air-circulating drier, sieved by using a mesh having an opening of 75  $\mu$ m, and thus [Toner 11] is obtained.

[0121]

[Comparative example 5]

(1) Synthesis of organic fine particle emulsion 2

Into a reaction vessel with a stirrer and a thermometer, 683 parts of water, 3 parts of sodium salt of methacrylic acid-ethylene oxide adduct sulfuric acid ester (Eleminol RS-30, manufactured by Sanyo Chemical Industries, Ltd.), 83 parts of styrene, 83 parts of methacrylic acid, 110 parts of butyl acrylate and 1 part of ammonium persulfate are charged, and agitated at 400 revolutions/minute for 15 minutes, and thus a white emulsion is obtained. A temperature in a system is increased up to 75 °C by heating to be allowed to react for 5 hours. Furthermore, 30 parts of 1 % ammonium persulfate aqueous solution are added, ripened at 75 °C for 5 hours, and thus an aqueous dispersing liquid [Resin fine particle dispersing liquid 2] of vinyl type resin (copolymer of sodium salt of styrene-methacrylic acid-butyl acrylate-methacrylic acid-ethylene oxide adduct sulfuric acid ester) is obtained. A weight average particle diameter obtained by measuring the [Resin particle dispersing liquid 2] by LA-920 is 520 nm. A part of [Resin fine particle dispersing liquid 2] is dried, and a resin portion is separated.

[0122]

(2) [Toner 12] is obtained similar to example 1 except for using the [Resin fine particle dispersing liquid 2] instead of the [Resin fine particle dispersing liquid 1] in example 1.

[0123]

Into 100 parts of the toner obtained from each example and

each comparative example as described above, 1.0 part of hydrophobic silica and 0.3 parts of hydrophobicized titanium oxide are mixed with a Henschel mixer. An obtained toner physical property value is shown in Table 1.

5        A developing agent including 5 wt% of toner subjected to an external agent treatment and 95 wt% of copper-zinc ferrite carrier having an average particle diameter of 40  $\mu\text{m}$  provided by coating a silicone resin is prepared, and continuous printing is performed by using imagioNeo450 manufactured by Ricoh Company, Ltd. corresponding to ZESM (Energy-conservation standards corresponding to a zero emission standby mode in a technical procurement program of a next-generation copier in a DSM (Demand-Side Management) program of 1999 International Energy Agency (IEA)) which may print 45 sheets of A4 size per minute, and an evaluation is performed based on the standard as described below. Results are shown in Table 2.

[0124]

(Evaluation items)

(a) Particle diameter

20        A toner particle diameter is measured at an aperture diameter of 100  $\mu\text{m}$  by using a particle size analyzer "Coulter Counter TA" manufactured by Coulters Electronics, Inc. A volume average particle diameter and a number average particle diameter are obtained from the particle size analyzer.

25        [0125]

(b) Charge quantity

A charge quantity is obtained by metering 6g of developing agent, charging it into a sealable metallic column and blowing it. Toner density is adjusted to 4.5 to 5.5 wt%.

30        [0126]

(c) Fixing property

By using imagioNeo450 manufactured by Ricoh Company, Ltd., an adjustment is performed such that toner of  $1.0 \pm 0.1 \text{ mg/cm}^2$

may be developed as a solid image on a transfer sheet of plain paper and thick paper (type 6200 manufactured by Ricoh and a copy printing sheet <135> manufactured by NBS Ricoh <135>), and a fixing belt temperature is adjusted to be variable, and a  
5 temperature at which no offset is produced is measured according to the plain paper, and a fixing lower limit temperature is measured according to the thick paper. The fixing lower limit temperature is defined as a fixing roll temperature at which a residual ratio of image density after rubbing an obtained fixing  
10 image with a putt becomes 70 % or more.

[0127]

(d) Degree of circularity

A degree of circularity is metered by using a flow particle image analyzer FPIA-2100 (manufactured by TOA Medical Electronics  
15 Co., Ltd.). A specific measuring method is described such that 0.1 to 0.5 ml of surface active agent as a dispersing agent, preferably, an alkylbenzenesulfonic acid salt is added to 100 to 150 ml of water provided by removing an impurity beforehand in a vessel, and a degree of 0.1 to 0.5 g of a measuring sample is  
20 further added. A suspension provided by dispersing the measuring sample is subjected to a dispersing treatment for 1 to 3 minutes or the like by using a supersonic disperser, a dispersing liquid concentration is provided to be 3000 to 10000 pieces/ $\mu$ l, and a toner shape and a distribution are measured by using the analyzer.

25 [0128]

After continuously running an image chart having a 5 % image area up to 100000 sheets, the evaluation as described below is performed.

(f) Image density

30 Image density is measured by X-Rite (manufactured by X-Rite, Inc.) after outputting a solid image. A measurement is performed on 5 points for each color independently, and an average is obtained according to each color.

[0129]

(g) Background stain

Background stain is measured by stopping a blank image during development, a tape transfer is performed for a developing agent on a photoconductor after development, and a difference from image density of an untransferred tape is measured by using 938 Spectrodensitometer (manufactured by X-Rite, Inc).

[0130]

(h) Cleaning property

A transfer residual toner on a photoconductor provided by passing a cleaning step is moved on blank paper by using a Scotch tape (manufactured by Sumitomo 3M Co., Ltd.), and a sample is measured by Macbeth reflection densitometer RD514 model. The sample is evaluated to be O (favorable) to be 0.01 or less as a difference from a blank, and X (unfavorable) to be over 0.01.

[0131]

(i) Filming

Presence or absence of toner filming produced on a development roller or a photoconductor is observed. An evaluation is performed by defining that a mark O indicates no filming,  $\Delta$  indicates presence of stripe-like filming, and X indicates presence of filming as a whole.

[0132]

[Table 1]

List of toner characteristics

	Toner No.	Toner particle diameter distribution			Toner shape Degree of circularity	Toner visco-elasticity G' (180°C)	Fixing property	
		Volume average particle diameter Dv(μ)	Number average particle diameter Dn(μ)	Dv/Dn			Fixing lower limit temperature (°C)	Hot offset generating temperature (°C)
Ex 1	Toner 1	6.05	5.78	1.05	0.95	2180	145	240°C or higher
Ex 2	Toner 2	5.62	5.22	1.08	0.94	1020	130	240°C
Ex 3	Toner 3	6.24	5.74	1.09	0.92	2470	150	240°C or higher
Ex 4	Toner 4	6.54	5.72	1.14	0.96	4380	160	240°C or higher
Ex 5	Toner 5	5.80	5.15	1.13	0.93	3520	155	240°C or higher
Ex 6	Toner 6	5.15	4.51	1.14	0.94	3880	160	240°C or higher
Ex 7	Toner 7	6.69	5.52	1.21	0.95	5430	165	230°C
ComEx 1	Toner 8	6.30	5.63	1.12	0.98	4400	190	230°C
ComEx 2	Toner 9	6.52	5.26	1.24	0.96	3560	175	225°C
ComEx 3	Toner 10	5.26	4.61	1.14	0.92	470	120	160°C or less
ComEx 4	Toner 11	7.82	6.52	1.20	0.98	10850	185	240°C or higher
ComEx 5	Toner 12	7.24	3.92	1.85	0.98	1950	145	180°C or less

[Abbreviation] Ex: Example, ComEx: Comparative example

[0133]

[Table 2]

	Toner No.	Toner charge quantity (-μC/g)			Image density			Background stain			Cleaning			Film-ing	Overall Evaluation
		S	10	100	S	10	100	S	10	100	S	10	100	100	
Ex 1	Toner 1	33.5	30.1	30.6	1.43	1.45	1.43	0.00	0.01	0.00	O	O	O	O	O
Ex 2	Toner 2	28.3	26.5	24.5	1.46	1.45	1.44	0.01	0.02	0.02	O	O	O	O	O
Ex 3	Toner 3	34.2	31.9	29.6	1.42	1.40	1.39	0.00	0.00	0.02	O	O	O	O	O
Ex 4	Toner 4	35.3	32.4	31.2	1.41	1.44	1.42	0.00	0.00	0.01	O	O	O	O	O
Ex 5	Toner 5	35.1	33.1	31.0	1.39	1.41	1.42	0.00	0.00	0.00	O	O	O	O	O
Ex 6	Toner 6	34.6	32.6	30.5	1.42	1.38	1.41	0.01	0.00	0.01	O	O	O	O	O
Ex 7	Toner 7	38.3	35.8	33.1	1.35	-	-	0.00	0.00	0.01	O	O	O	O	O
ComEx 1	Toner 8	32.5	-	-	1.28	1.44	-	0.02	-	-	X	-	-	-	X
ComEx 2	Toner 9	34.6	16.7	-	1.36	-	-	0.02	0.41	-	O	O	-	-	X
ComEx 3	Toner 10	21.0	-	-	1.43	-	-	0.01	-	-	O	-	-	-	X
ComEx 4	Toner 11	39.1	-	-	1.33	-	-	0.00	-	-	X	-	-	-	X
ComEx 5	Toner 12	30.1	-	-	1.33	-	-	0.00	-	-	X	-	-	-	X

5 [Abbreviation] S: Start, 10: After 10000 sheets, 100: After 100000 sheets, Ex: Example, ComEx: Comparative example

[0134]

The toners 8, 9, 10, 11 and 12 have a fixing failure and continuous printing may not be performed, and an evaluation is discontinued. The toner 9 is observed to produce a trace amount of fixing failure, and continuous printing may not be performed by worsening of background stain due to a decrease in charge after printing 10,000 sheets, and an evaluation is discontinued.

[0135]

15 [Effects of the Invention]



According to the present invention, such negative charging toner may be provided that the toner has a stable negative charge property, and therefore provides excellent printing quality at an initial stage, excellent stability of a sharp image in continuous printing, a stable cleaning property, an excellent offset proof property, and an excellent low-temperature fixing property in which filming contamination relative to a photoconductor, a developing roller or the like is prevented.

Moreover, according to the present invention, a developing agent containing the toner, an image forming method using the developing agent, a container filled with the developing agent, and an image forming apparatus loaded with the container may be provided.

#### [Brief Description of the Drawings]

[Fig. 1] Fig. 1(a) is an explanatory diagram showing one example of a spindle-shaped toner particle. Fig. 1(b) is an explanatory diagram for a long axis  $r_1$ , a short axis  $r_2$  and thickness  $r_3$  of a spindle-shaped toner particle.

#### [Name of Document] Abstract of the Disclosure

#### [Abstract]

#### [Objectives of the Invention]

An object of the present invention is to provide toner having a sharp charge quantity distribution of a toner negative charge property and capable of forming a clear and excellent visible image over a long period of time. Moreover, another object of the present invention is to provide toner supporting a low-temperature fixing system while maintaining a cleaning property having an excellent offset proof property without contaminating a fixing device and an image.

#### [Means for Achieving the Objectives]

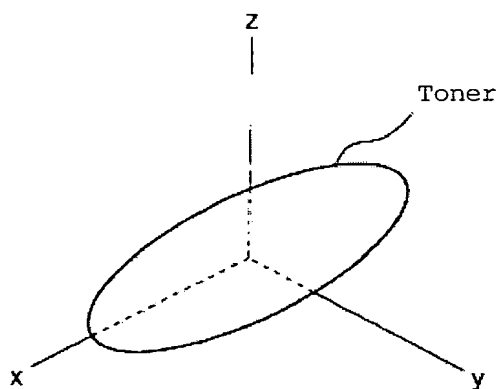
Negative charging toner according to the present invention is obtained by dissolving or dispersing a toner composition containing a toner binder resin including a modified polyester

type resin (i) reactible with an active hydrogen in an organic solvent to provide a dissolved product or a dispersed product, dispersing the dissolved product or the dispersed product in an aqueous medium containing a resin fine particle, and

- 5 simultaneously causing the toner composition to react with a cross-linking agent and/or an extension agent, and removing the solvent from an obtained dispersing liquid, and a storage modulus ( $G'$ ) of the toner at a frequency of 1 Hz and a temperature of 180 °C is 500 Pa or more.

10 [Selected Drawing] None  
[Name of Document] Drawing  
[Fig. 1]

(a)



(b)

